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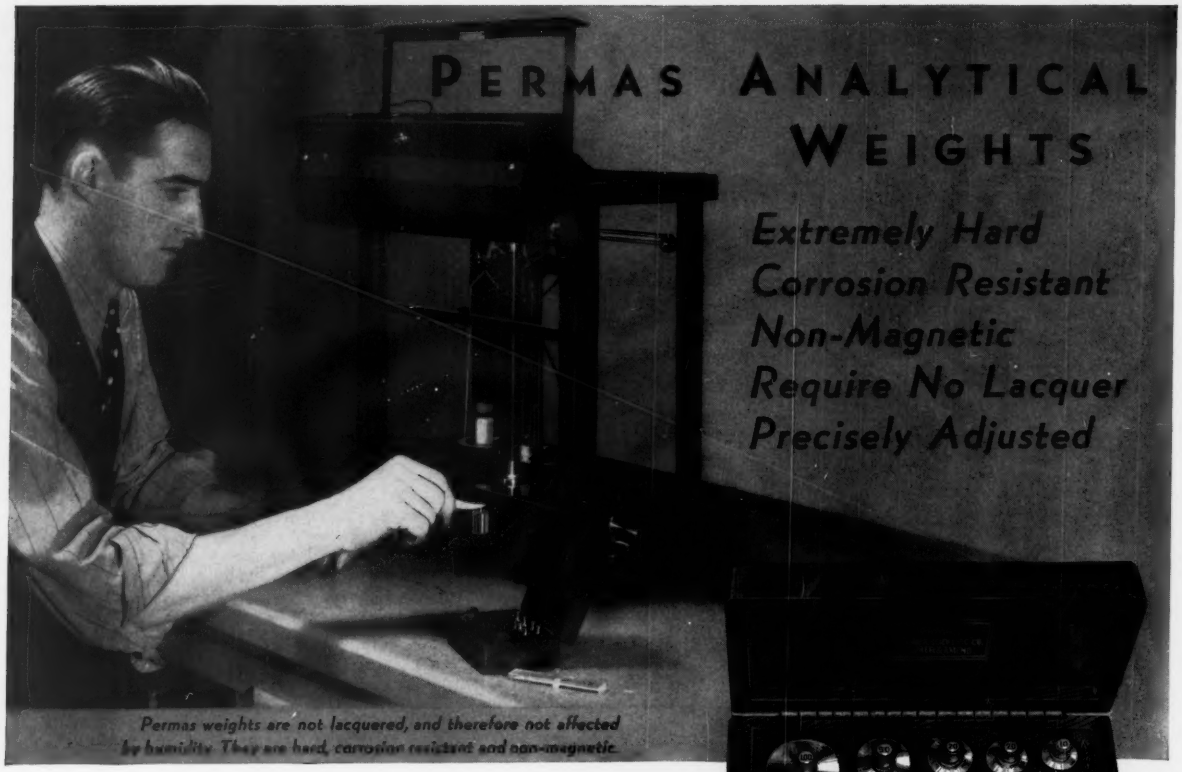
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Frontispiece—Chemical Warfare Agents XIII

Editor's Outlook 201

What's Been Going On 202

The Vitamins, *C. R. Addinall* 203

A Simple Sodium Press for the Small Laboratory, *Walter C. Beard, Jr.* 214

The Old Tungsten Mine at Long Hill, Connecticut, *Frederick H. Getman* 215

Apparatus for Semimicro Filtration, *Jacob Cornog and Floyd O. Krause* 217

Carbonyl Compounds as Oxidizing Agents, *Homer Adkins* 218

The Indicator Method of Classifying Acids and Bases in Qualitative Organic Analysis, *David Davidson* 221

Construction of Complex Molecular Models with Application to Carbohydrates, *Richard S. Bear* 227

Lecture Experiment on the Synthesis and Combustion of Ammonia, *F. W. Fromm* 230

Electrical Properties of Solids, Part II, *Raymond M. Fuoss* 231

Formula of the Month 235

A Device to Demonstrate Electronic Transfer in Redox Reactions, *Luis F. LeRoy* 236

A Method of Teaching Thermodynamic Functions, *Harold Becher* 237

Phase Models for Ternary Systems, *Paul Porter Sutton* 238

High-School Chemistry
Liquid Glass and Solid Solutions, *C. H. Jeglum* 239

Letters 243

Fourth Summer Conference of the New England Association of Chemistry Teachers, Preliminary Announcement 244

Correction 244

Out of the Editor's Basket 245

Summer Courses in Microchemistry at Cornell University 247

Recent Books 248

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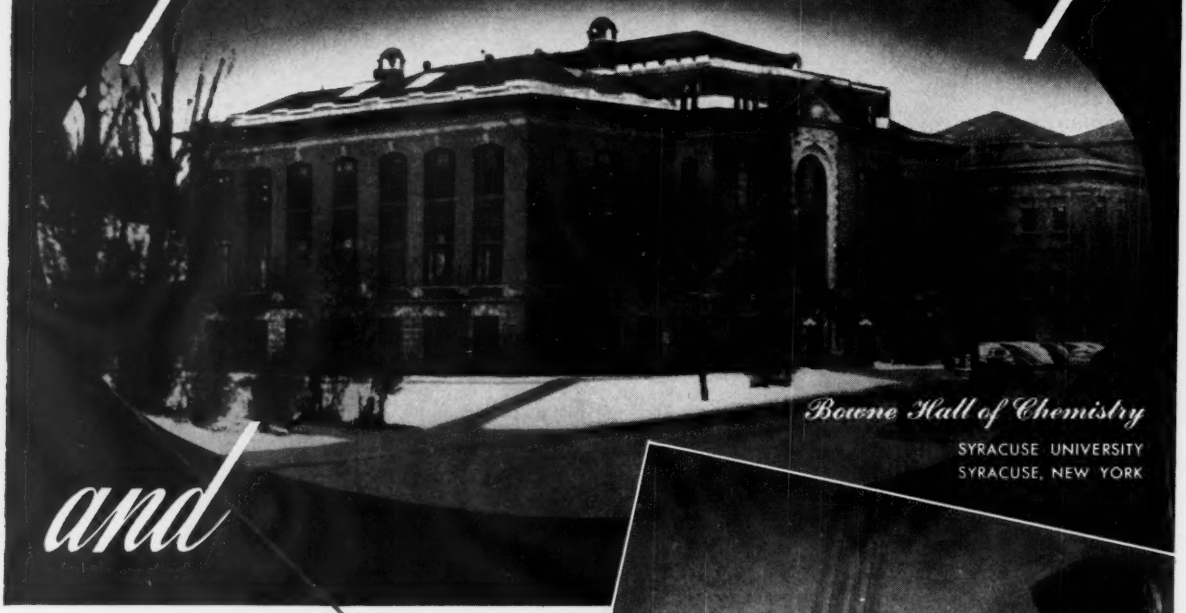

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CHEMICAL WARFARE AGENTS

REFERENCE AND TRAINING CHART

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CLASS	NAMES AND SYMBOLS	FORM	ODOR	PHYSIOLOGICAL EFFECT	TACTICAL CLASS	PROTECTION	FIRST AID [After removal from gassed area]	PERSISTENCE	FIELD NEUTRALIZATION
VESICANTS	MUSTARD $S(CH_2CH_2)_2Cl_2$ DI CHLORETHYL SULFIDE	LIQUID AND VAPOR	Garlic, Horseradish, Mustard	Delayed effect. Burns skin or membrane. Inflammation respiratory tract leading to pneumonia. Eye irritation, conjunctivitis.			Undress; remove liquid mustard with protective ointment, bleach paste, or kerosene; bathe; wash eyes and nose with soda solution.	One day to one week. Longer if dry or cold.	Cover with unslaked lime and earth. 3% solution of Na_2SO_3.
VESICANTS	LEWISITE $CHCICH\text{-}AsCl_2$ CHLORVINYL-DICHLORARSINE	LIQUID AND VAPOR	Geraniums	Burning or irritation of eyes, nasal passages, respiratory tract, skin: Arsenical poison.			Undress; remove liquid Lewisite with hydrogen peroxide, lye in glycerine, or kerosene; bathe; wash eyes and nose with soda. Rest—Doctor.	One day to one week. Longer if dry or cold.	Wash down with water. Cover with earth. Alcohol. NaOH spray.
VESICANTS	ETHYLDICHLORARSINE $C_2H_5\text{-}AsCl_2$	LIQUID AND VAPOR OR GAS	Stinging, like pepper in nose	Causes blisters, sores, paralysis of hands, vomiting. Severe on long exposure.			Undress; remove liquid with hydrogen peroxide, lye in glycerine, or kerosene; bathe; wash eyes and nose with soda. Rest—Doctor.	One hour.	Cover with earth, caustic.
LUNG IRRITANTS	CHLORINE Cl_2	GAS	Highly Pungent	Lung irritant.			Remove from gassed area. Keep quiet and warm. Coffee as stimulant.	10 minutes.	Alkaline solution.
LUNG IRRITANTS	CHLORPICRIN CCl_3NO_2 NITROCHLOROFORM	GAS	Flypaper, anise	Causes severe coughing, crying, vomiting.			Wash eyes, keep quiet and warm. Do not use bandages.	Open 6 hours. Woods 12 hours.	Na_2SO_3—Sodium sulfite in alcohol solution.
LUNG IRRITANTS	DIPHOSGENE $ClCOOC\text{-}Cl_3$ TRICHLORMETHYL CHLOROFORMATE	GAS	Ensilage, Acrid	Causes coughing, breathing hurts, eyes water, toxic.			Keep quiet and warm. Give coffee as a stimulant.	30 minutes.	Alkali.
LUNG IRRITANTS	PHOSGENE $COCl_2$ CARBONYL CHLORIDE	GAS	Musty hay, Green corn	Irritation of lungs, occasional vomiting, tears in eyes, duped feeling. Occasionally symptoms delayed. Later, collapse, heart failure.			Keep quiet and warm, bed rest. Coffee as a stimulant. Loosen clothing. No alcohol or cigarettes.	10 to 30 minutes.	Alkali.
LACRIMATORS	CLORACETOPHENONE $C_6H_5CO\text{-}CH_2Cl$	GAS	Apple Blossoms	Makes eyes smart. Shut tightly. Tears flow. Temporary.			Wash eyes with cold water or boric acid solution. Do not bandage. Face wind. For skin, sodium sulphite solution.	15 minutes.	Strong, hot solution of sodium carbonate.
LACRIMATORS	BROMBENZYLCYANIDE $C_6H_5CH\text{-}BrCN$	GAS	Sour fruit	Eyes smart, shut, tears flow. Effect lasts some time. Headache.			Wash eyes with boric acid. Do not bandage.	Several days. (Weeks in winter.)	Alcoholic sodium hydroxide spray.
STERNUTATORS	ADAMSITE $(C_6H_5)_2\text{-}NHAsCl$ DIPHENYLAMINECHLORARSINE	GAS	Coal Smoke	Causes sneezing, sick depressed feeling, headache.			Keep quiet and warm. Loosen clothing. Reassure. Spray nose with neo-synephrin or sniff bleaching powder. Aspirin for headache.	10 minutes.	Bleaching powder solution.
STERNUTATORS	DIPHENYLCHLORARSINE $(C_6H_5)_2\text{-}AsCl$	SMOKE	Shoe Polish	Causes sick feeling and headache.			Remove to pure air, keep quiet. Sniff chlorine from bleaching powder bottle.	Summer 10 minutes.	Bleaching powder solution.
SMOKES	H C MIXTURE $ZN + C_2Cl_6$	SMOKE	Sharp Acrid	Harmless.		None needed.	Produces no effect requiring treatment.	While burning.	None needed.
SMOKES	SULPHUR TRIOXIDE $SO_3 + SO_3HCl$ IN CHLOSULFORIC ACID	SMOKE	Burning matches	Causes prickling of skin, flow of tears.			Wash with soda solution.	5 to 10 minutes.	Alkaline solution.
SMOKES	TITANIUMTETRACHLORIDE $TiCl_4$	SMOKE	Acrid	Harmless.		None needed.	Produces no effect requiring treatment.	10 minutes.	None needed.
INCENDIARIES	WHITE PHOSPHORUS P	SMOKE	Burning matches	Burning pieces adhere to skin, clothing.		None needed.	Pack in cloths wet with copper sulphate (blue vitriol) or water or immerse in water. Pick or squeeze out particles. Treat for burn.	10 minutes.	Burns out.
INCENDIARIES	THERMIT $8Al + 3Fe_3O_4$	INCENDIARY	None	5,000 degree heat ignites materials.		None needed.	Treat for severe burn.	5 minutes.	Quickly cover with earth or sand.

GENERAL INSTRUCTIONS

The importance of proper first aid for gas victims cannot be overemphasized. The following are general rules which apply in all cases.

A. Act promptly and quietly; be calm.

B. Put a gas mask on the patient if gas is still present or, if he has a mask on, check to see that his is properly adjusted. If a mask is not available, wet a handkerchief or other cloth and have him breathe through it.

C. Keep the patient at absolute rest; loosen clothing to facilitate breathing.

D. Remove the patient to a gas-free place as soon as possible.

E. Summon medical aid promptly; if possible, send the victim to a hospital.

F. Do not permit the patient to smoke, as this causes coughing and, hence, exertion.

KEY

- HOSPITAL CASE
- FIRST AID TREATMENT
- SMOKE
- INCENDIARY
- MASK PROTECTION NEEDED
- FULL PROTECTIVE CLOTHING NEEDED

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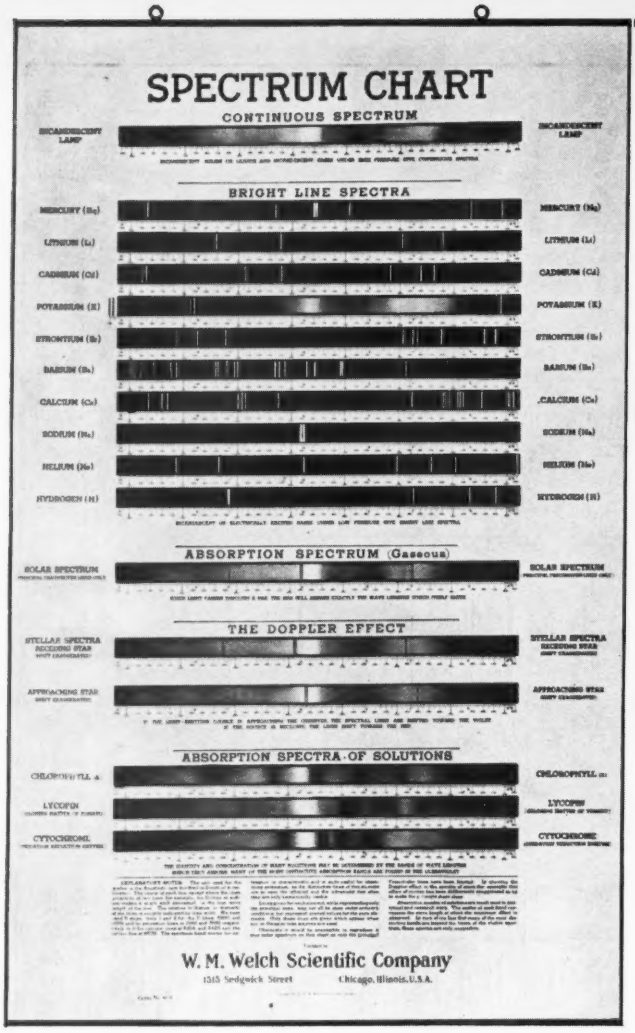

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Below are two spectra with these same lines shifted, one for the spectrum of a receding star, the other for an approaching star. Finally, three absorption spectra for Chlorophyll, Lycopin and Cytochrome over the visible range of wave lengths are shown to illustrate the application of Spectroscopy to the study of vegetable and organic compounds. Printed in seven colors and black on heavy chart paper with metal strips top and bottom.

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Editor's Outlook

PERHAPS it's just as well that we were getting a trifle suspicious of "the good old days," for they are evidently gone now—for better or for worse. The sooner we become convinced that there will be no more business as usual for a long time to come, but that the whole structure of our lives is to be uprooted and laid down in new patterns, the better. No longer can we do what we please, have the things we want, scarcely hope for the ideals to which we aspire. And we are already becoming more or less content with this state of affairs—which is a good sign, for it is the only state of affairs which can possibly bring us to safety. Eliminate waste, take up the slack wherever possible, find quicker, easier, more efficient ways of doing the necessary job. There is no doubt but that this country faces the greatest crisis in its history, and much of what we will learn under this compelling pressure will doubtless stay with us after the crisis is passed. If there is any incidental virtue in war whatever, it is that it requires us to face issues squarely and to get down to the bare fundamentals. Our vision, in some directions at least, may be actually sharpened.

Which certainly has a bearing on the structure and content of our educational system. We are probably going to learn—in fact, are already beginning to learn—some disturbing things about our educational theories and practices.

Not long ago the United States Commissioner of Education made the statement that the emphasis in education has shifted from "an opportunity to learn" to "forced training." We always liked the leisurely implications of the opportunity to learn but must confess that the present seems no time to indulge the luxury of deciding for oneself when, where, and how much to work. We do hope to return to this, and perhaps some other luxuries, if and when the elements of our still-lingering high standard of living are re-attained. Meantime, we must coach as many people as possible in the skills which they must acquire if we are to maintain our freedom.

One of the disturbing things we are learning is the evident insufficiency of our technical education. Thus far, at least, this has shown itself to be quantitative rather than qualitative. In other words, it is another one of the many shortages of strategic materials, and an especially important one. It will be no new idea to readers of this page that the country has too few chemists, physicists, engineers, scientists, and technicians of all kinds.

This war has been described (by an eminent chemist) as a physicist's war. But not only are there too few physicists to fight it but the prospect of training enough to do so is very slim. The American Institute of Physics recently issued a statement outlining the difficulties of the situation. The army has an urgent need for 100,000 trained radio and electronics experts. Filling this need calls for a large reservoir of men capable of receiving this and other technical training. It might indeed be possible to find such a number, but where to find enough properly qualified teachers is another matter. There are certainly not enough college instructors for the purpose—even if we could be sure that they would be left on the job. Obviously, the next place to look is in the high schools. But it appears that the great majority of high-school teachers of physics simply are not prepared to meet this emergency. Their own preparation in the subject matter of physics is entirely inadequate to prepare them to carry on any training program in advanced physics. The statement goes on to recommend that more students be given a broader background in science and mathematics in high school, and that an effort be made to rectify the teacher situation by increasing the amount of subject matter study required in the preparation of prospective secondary-school physics teachers. There is no assurance, of course, that such late measures will be timely enough to do any good, but certainly nothing less should be contemplated.

This dilemma of our colleagues in physics is uncomfortably close to home. Let us not gloat over their difficulty, for there is scarcely a doubt but that it would be equally the case in chemistry if we were the ones put on the spot.

The greater emphasis upon mathematics and the physical sciences at the high-school level is already being encouraged and will probably call forth a vigorous response. It will be a challenge to science education to see that this revival of interest is maintained and made to outlast the war stimulus.

The question of a technological "High Command" has been ably discussed in a recent number of *Fortune*, and it is sobering to observe that the whole country has turned to science and technology for its salvation. If science fails in this crucial test there are hard days ahead for literature and the arts—all the humanities, in fact. It is a responsibility and privilege shared by every participant in our program of science education, from the top to the bottom.

On the other hand, there are many who would have us believe that science itself is responsible for the world's present troubles; that war has come because of the invention of more effective weapons and means of carrying it on. But you don't bump your neighbor off merely because you can now buy a gun that shoots straighter and farther than any before; you do it because you want to steal his new tires, or because he has swindled you out of a week's pay, or just because you fly off the handle easily and don't like the shape of his nose, the color of his face, or the way he makes eyes at your wife.

Even before we are properly in this war we are wondering about the shape of things to come after. Perhaps now, before we are too exhausted, is really a good time to make resolutions for the future. At any rate, we must be sure that *this* war teaches us the fatal dangers of isolationism, unpreparedness, and overconfidence. Our whole national life must be reshaped to make us strong and able to protect our freedom and democracy without the wasteful confusion that has twice within a short time led us to the brink of disaster. And our educational system, in this as in every other important issue, will be one of the largest factors.

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What's Been Going On

A PLANT is being installed in Brazil to extract the oil from tomato seeds.

Fiberglas is being used as an insulating material in the hulls of battleships and around the oil tanks of bombers.

In the preservation of fruit, sulfur dioxide serves as an antioxidant and as an aid in the preservation of both color and vitamin C.

The chemical research laboratories of the United States have produced over 200,000 commercial products since 1914.

Cellophane now has more than 5000 uses in packaging, and the present shortage of tin will materially increase the demand for cellophane, pliofilm, and similar products.

The total crude petroleum reserves at the beginning of 1941 were estimated at 19,025,000,000 barrels. Our refining capacity seems to be adequate for immediate demands, about one-third of the refining installations being less than four years old.

As a result of the wide use of cracking in the petroleum industry, the conservation of crude oil amounts to about 1,865,000,000 barrels annually, which is approximately one-half of the consumption.

In certain cases the hardness or softness of a plastic depends on the heat treatment it receives in processing.

Antiknock performance on the road does not necessarily correlate with octane rating, according to tests run over a period of three years on about 200 commercial fuels in twenty-five different cars, under the sponsorship of Pure Oil Company and Ethyl Gasoline Corporation.

Sweetening gasoline by solvent extraction, developed by Mason of the Atlantic Refining Company, not only deodorizes the gasoline but increases its susceptibility to lead tetraethyl, and thus indirectly improves the octane rating of the fuel.

The traffic in vitamins last year amounted to $100,000,000, yet just two decades ago the nature of these dietary essentials was unknown.

There is some evidence that histamine, which stimulates the autonomic nervous system, may be responsible in part for some of the symptoms of hay fever and other allergies, according to Katz and Cohen of Tulane University.

Recent studies have indicated that methyl bromide may be used economically and effectively as a flour-mill fumigant.

The treatment of wood with chromated zinc chloride not only protects the wood from decay and termite attack but also reduces the fire hazard.

A patent issued to Peck and Gaylor, and assigned to Standard Oil Development Corporation, claims that the accumulation of carbon in the cylinder of an engine can be reduced to a minimum by a coating of zinc oxide.

An ointment containing five per cent of very finely divided sulfathiazole has been found to be effective when applied to such skin diseases as acne, impetigo, infected eczema, and boils, according to studies by Keeney, Pembroke, Chatard, and Ziegler, reported in the *Journal of the American Medical Association*.

Pentothal sodium, an anesthetic which is administered by a "shot" in the arm, is successfully replacing laughing gas for dental operations, according to Dr. Olson of Hollywood. "The recovery period is 10 to 15 minutes without any symptoms of sickness at the stomach, and the patient will open the mouth when told to, but later on will have no recollection of having done so."

Waste gases from the steel and petroleum industry are being fractionated at low temperatures in Russia, and the purified constituents then used for the syntheses of high-octane gasoline, rubber, and other products.

The production of starch from glucose has been effected by enzymatic synthesis at the University of California.

Manganese salts are universal constituents of plants and animals, but our knowledge of the metabolism of manganese is yet very meager.

Ammonium sulfamate, recently introduced on the market, is not only an effective flameproofing agent for cloth, paper, and insulating materials, but also a good herbicidal chemical for the extermination of certain deep-rooted perennials such as Canadian thistle, chokecherry, dew berry, dock, hoary cress, poison ivy, poison oak, ragweed, Russian thistle, sow thistle, wild blackberry, and miscellaneous noxious annual weeds.

Nylon bristles, because of their superior qualities, are to be used in the production of brushes for cleaning guns.

The sixth commandment for the treatment of compound fractures, according to Thompson in the November, 1941, issue of the *Journal of the American Medical Association*, is "coat the wound with sulfanilamide or one of its derivatives."

A fermentation process has been developed, at the Northern Regional Research Laboratory, which yields alcohol, butanediols (about 60 per cent), and glycerol. The butanediols are converted into butadiene, which may be polymerized in turn to give a good grade of synthetic rubber. It is believed that the process will be in commercial production before the end of the year. The dream of corn to rubber is, accordingly, all but realized industrially.

Gulf, Magnolia, Pure Oil, Socony Vacuum, and Texas Oil companies are considering plans for the production of 50,000 tons of butadiene annually. In America, butadiene is best produced from (*a*) butane, or (*b*) butylene. In Europe, it is best produced from vinyl acetylene or aldol, the former being produced from acetylene and the latter from acetaldehyde.

Paper made from clay, which can be written or printed on, can be brought to a white heat without being destroyed, and is resistant to attack by acid, alkali, and oil.

The soybean and research have produced useful oil for the paint industry, plastics for numerous uses, and now from a new pilot plant come 1000 pounds of synthetic fiber per day. The next contribution of the soybean may be a type of synthetic rubber.

The National Defense program is aiming at an *increase* in the production of steel by 3,000,000 tons, of synthetic rubber by 400,000 tons, of aluminum by 400,000 tons, of zinc by 350,000 tons, of imported nickel by 6000 tons, of tungsten by 10,000 tons, of chromite by more than 5000 tons, of manganese by over 10,000 tons, of lead by 400,000 tons, of tin by more than 100,000 tons, and of synthetic fibers by 100,000 tons. These figures seem colossal, but America usually does the job that it has to do.

It is estimated that the production of several important by-products from cranberry seeds and skins may add a million dollars annually to the value of the cranberry crop of the United States. A pilot plant is producing ursolic acid from the skins at the rate of about two pounds per day, the seeds contain an oil which has 200 units of vitamin A per gram of oil, and the dried skins have been ground and mixed with a binder and molded into a plastic, which has properties similar to cork.

Lignin, which is obtainable from corn cobs and other plant wastes, offers another approach to the purification of water. When one part of lignin is added to one million parts of water and the mixture passed through normal sand filters, both iron and magnesium are removed.

The marketed production of liquefied petroleum gas during 1941 amounted to about 445,000,000 gallons as compared to 313,456,000 gallons for 1940. These figures include liquefied propane, butane, propane-butane mixtures, and pentane.

To loosen frozen stopcocks, C. T. Taylor suggests that they be soaked two to twenty-four hours in a solution containing one ounce of Aerosol OT (du Pont) per liter of water.

Metalox is a powder, containing iron, which is used to accelerate the setting time of cement. Surface scaling is decreased by the addition of traces of synthetic resins.

Fluffo is a new vegetable shortening. At each level of fat intake, however, it has been found that lard has greater digestibility than does hydrogenated cottonseed oil.

—Ed. F. Degering

The Vitamins

C. R. ADDINALL, PH.D. *Merck and Co., Inc., Rahway, New Jersey*

DISCOVERY AND NATURE OF VITAMINS

THE diseases, scurvy, rickets, beriberi, and pellagra are widely spread in all parts of the world and have been known throughout recorded medical history. Beriberi was described in China as early as 2600 B.C.; the privateer, Sir James Lancaster, introduced the use of oranges, lemons, and lemon juice for the cure of scurvy among the crews of the ships of the East India Company from 1601 onward; and Schuette in 1824 attributed the potency of cod-liver oil in the treatment of rickets to an imponderable amount of substances which could not be determined by the chemist. It was, however, only recently that it was realized that these diseases are caused by the lack of small amounts of essential substances in the daily diet and that vitamins were recognized as these physiological essentials.

Our present-day knowledge of the vitamins has been acquired as the result of the efforts of very many investigators, each of whom has advanced a little further than some other pioneer, often reaching his goal after setting out from a far different starting point so that, today, it is impossible to do even-handed justice to the various contributions in the field. Probably, however, the first clear evidence for the existence of dietary factors of the nature of vitamins came in 1881 from the work of N. Lunin in Switzerland, who found that a natural substance like milk must contain, besides proteins, sugars, fats, and minerals, small quantities of unknown substances essential to life. Some time later, this finding was elaborated by Pekelharing of Holland who, more than thirty years ago, gave a clear statement of the vitamin doctrine and demonstrated for the first time the existence of diseases due to deficiencies in the diet when he pointed out that

> "there is still an unknown substance in milk which even in very small quantities is of paramount importance in nutrition. If this substance is absent, the organism loses the power properly to assimilate the well-known principal parts of food, the appetite is lost and, with apparent abundance, the animals die of want. Undoubtedly this substance occurs not only in milk but in all sorts of foodstuffs both of vegetable and animal origin."

About this time, Hopkins—the spiritual father of the vitamin doctrine—concluded from similar experiments that milk contains "accessory food factors."

The tropical wasting disease, beriberi, had been eradicated from the Japanese Navy by Takaki in 1882, by adding more meat and vegetables to the sailors' diet and by replacing the customary rice by wheat and barley. Similar governmental concern led to the investigation of the disease in the Dutch East Indies by the Netherlands Government and resulted in Eijkman's coming to the conclusion that beriberi resulted from the consumption of polished rice and to the discovery of the striking fact that fowls fed on polished rice suffered from polyneuritis and could be cured by feeding them rice bran. His successor, Grijns, showed that the disease was caused, not by a poison, but by the lack of some essential nutrient contained in the rice bran

Courtesy of Merck and Co., Inc.

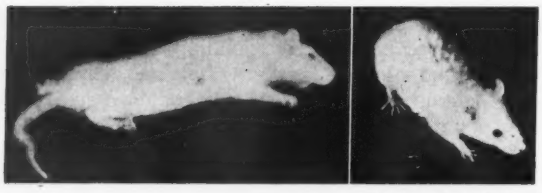
POLYNEURITIC PIGEON
Before treatment After treatment

discarded from the polished rice. For some ten years many investigators followed the leads of these striking observations and in 1911 the biochemist Funk, then working at the Lister Institute in London, attempted to isolate from rice bran the substance active in the cure of beriberi and succeeded in obtaining a crystalline fraction of material capable of curing polyneuritis in pigeons in doses of 20 milligrams. In July, 1912, he advanced the theory that beriberi, scurvy, possibly pellagra, and probably rickets were caused by the absence from the diet of "special substances which are of the nature of organic bases, which we will call vitamines." Funk's paper aroused world-wide interest. The magic properties of the "vitamine"—its potency in almost unbelievably small doses, the minuteness of the amount in our food, its indispensability, and, above all, its catch-word (*vita*, life; *amine*, a nitrogenous base)—all compelled attention. The question as to the existence of the corresponding scurvy vitamine, pellagra vitamine, and rickets vitamine, demanded an answer and, as will be seen, was answered more fully than could be dreamed of, within the peaceful years between the two World Wars.

In America, the nutritional studies of Osborne and Mendel (1911–13) on the relative value of various pure proteins in the feeding of rats had shown that butter contained a substance exerting a marked influence on growth. The scientific investigation of nutritional problems with reference to farm stock by McCollum and Davis (1913–14) led to an independent discovery of this growth-stimulating substance and to the further discovery that the unpurified sugar used in their diets contained a second essential growth-promoting factor. The two factors were termed "fat-soluble A" and "water-soluble B." It soon was shown that "water-soluble B" occurred in wheat germ, rice polishings, and yeast and was probably identical with the "antiberiberi vitamine." Previously, Holst and Frölich of Christiana, while endeavoring to produce beriberi in

guinea pigs by means of unbalanced diets, were surprised to find that scurvy and not beriberi resulted. They began pioneer work on this antiscorbutic, *i. e.*, "antiscurvy," factor which was named "water-soluble C." Later, Drummond proposed that the two systems of naming should be combined and the antiscorbutic factor was termed vitamin C, the terminal "e" being dropped to show that the factors were not necessarily amines. Evidence for the subdivision of the "fat-soluble A" into vitamin A and an antirachitic, *i. e.*, "antirickets," vitamin D gradually accumulated. In 1922, the existence of an antisterility factor, vitamin E, was reported by Evans and his co-workers in California and more recently, in 1935, Dam announced the existence of the anticoagulation factor, vitamin K (German, *Koagulation*).

It was understood that, as the new vitamins were discovered, they would be assigned succeeding letters in the alphabet, in rotation. Subsequent history has only gone to show how "the best laid schemes o' mice an' men gang aft agley." It was soon found that the so-called vitamin B was not a single principle but a complex containing a heat-sensitive, growth-promoting component—known today as vitamin B_1—requisite for the prevention of certain[1] symptoms in rats and pigeons, and a heat-stable, growth-producing complex necessary for the prevention of dermatitis, a skin disease, in rats. In contrast to the simple nature of the antineuritic vitamin B_1, which is unstable to heat, it has become evident that the thermostable component is an extremely complex mixture from which chemists have gradually managed to separate the pure chemical compounds, riboflavin, nicotinic acid, pyridoxine, and pantothenic acid, in addition to other less well-defined provisional factors—all of which are regarded as vitamins of the "B complex."



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POLYNEURITIC RAT

Before treatment After treatment

Thus it is seen that vitamins are organic substances relatively complex in structure and indispensable in very small amounts to the animal body which, however, usually lacks the capacity of synthesizing them from simpler substances and must obtain them from foods. Like the many accessories essential to the maintenance and running of an automobile, these accessory factors are absolutely essential to the growth and maintenance of the human body in good health and, similarly, as chemical compounds, have relatively little structural likeness. As Funk admitted, the name, vitamin, sounds well and serves as a catch-word, but it is not a strictly chemical classification.

Foodstuffs contain very minute amounts of the vitamins. For example, it is probable that one ton of rice bran contains less than one ounce of vitamin B_1, even if all could be extracted without loss. It is necessary for the chemist to isolate the vitamin in its pure form before he can study its structure and its chemical and physical properties, and make it available to the pharmacologist for studies of its effect on animals. Therefore, the first problem in vitamin investigations is always that of devising methods of extracting the vitamin from natural products such as fish oils, rice bran, liver, yeast, citrus fruits, peppers, wheat germ oil, alfalfa, etc. When, after laborious investigations, this has been accomplished, the pure material must be broken down and analyzed to determine its chemical structure so that methods may be worked out for the synthesis of large amounts of the vitamin from readily available and simpler chemical compounds. This cheaper and more available product is then placed at the disposal of pharmacologists who determine the physiological reactions of the vitamin in animals. Then, and only then, when its suitability for administration to human beings has been established, can the product be used by clinicians and physicians for studies of its effects on human beings. Afterward, when these studies are complete, the vitamins can be introduced into everyday use for the public good in the improvement of the daily diet under the guidance of authorities on nutrition. In the following paragraphs on the individual vitamins the tracing of these steps will be briefly indicated, and it will be evident how, gradually, it has become possible to make commercially available, in astonishingly large quantities, these nutritional substances so essential to human welfare, which a few short years ago were so vaguely defined. Since, historically, attempts at isolation were first made on vitamin B_1, the vitamins of the B complex will be considered first, followed by the water-soluble vitamin C and later by the fat-soluble vitamins A, D, E, and K.

THE WATER-SOLUBLE VITAMINS

Vitamins of the B Complex

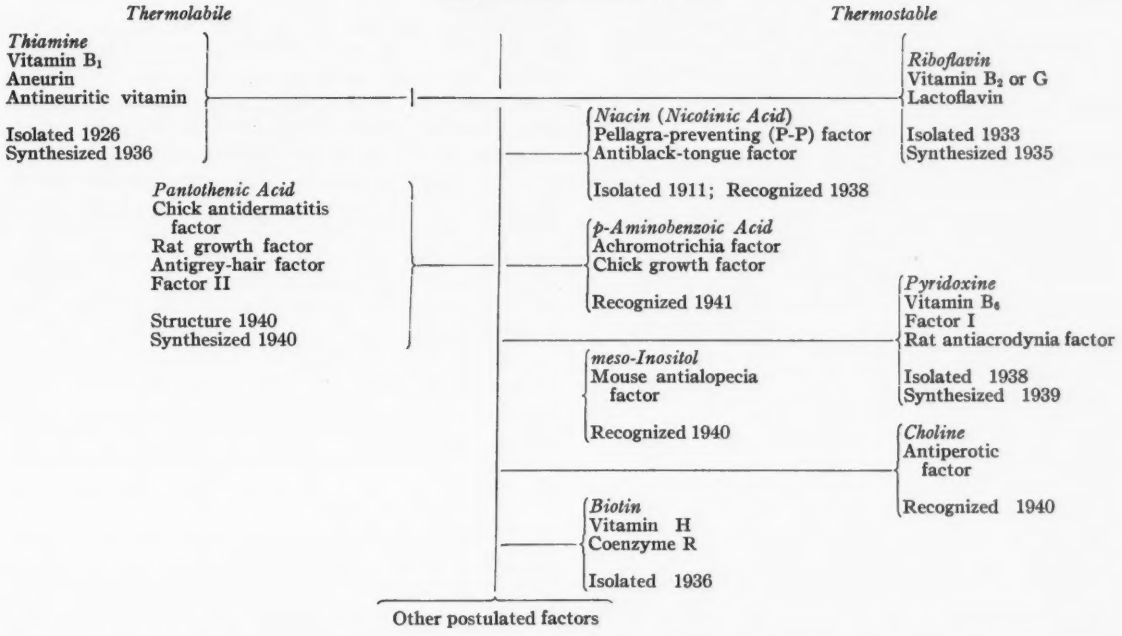
In the earlier investigations on the water-soluble vitamin substance present in foodstuffs such as liver, yeast, and rice bran, it was assumed that there was only one active principle. In 1920 it was shown that the aqueous extracts from these materials could be divided into two fractions, the thermolabile and thermostable components, depending on their susceptibility to destruction by heat. This division, like that of the further separation of the active principle into adsorbable and non-adsorbable fractions, is of historic interest and is convenient, but it is not precise since the stability and adsorbability of the various vitamins depend upon the acidity of the solutions in which they occur. Consequently, in the present chart of the vitamin B com-

[1] A condition known as polyneuritis.

VITAMIN B COMPLEX

LIVER, YEAST, RICE BRAN, ETC.

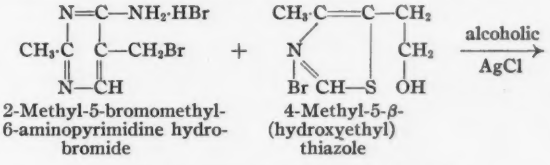
Supposed single entity 1899–1920



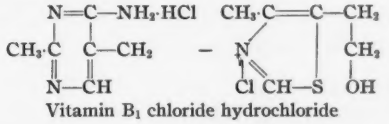
plex, pantothenic acid is recorded as a thermolabile component of the vitamin B complex, although other schemes list vitamin B_1 as the only thermolabile component. At the present time, the complex has been shown to consist of five major factors, namely vitamin B_1, riboflavin, nicotinic acid, pyridoxine, and pantothenic acid. There are also at least four lesser factors—inositol, choline, para-aminobenzoic acid, and biotin.

Vitamin B_1.—Vitamin B_1 (aneurin, thiamine, thiamin chloride, thiamine hydrochloride) is often referred to as the antineuritic vitamin since, in its absence, various symptoms of different forms of neuritis occur. After Eijkman's pioneering discoveries, many attempts were made to isolate the pure crystalline vitamin. It can be adsorbed[2] from its aqueous solutions by passage through layers of fuller's earth and removed by elution[2] with alkalies or solutions of strongly basic alkaloids such as those of quinine salts. It was by such isolation procedures that Jansen and Donath, working in Eijkman's original laboratory in Java, succeeded in isolating the first crystalline samples of vitamin B_1 in 1926, after some 17 years of continuous investigation. It was not until 1933 that the American chemist, R. R. Williams, obtained a sufficient quantity of the vitamin to make possible the explanation of its structure.

Williams discovered in 1935 that the vitamin is split quantitatively into two complete halves by the action of neutral sodium sulfite at room temperature. Extensive studies of the products of this remarkable reaction not only indicated the structure of the vitamin but pointed the way to its successful synthesis from the two substances, 2-methyl-5-bromomethyl-6-aminopyrimidine hydrobromide and 4-methyl-5-β-(hydroxyethyl)thiazole, by condensation and shaking with alcoholic silver chloride as shown:



2-Methyl-5-bromomethyl-6-aminopyrimidine hydrobromide + 4-Methyl-5-β-(hydroxyethyl) thiazole



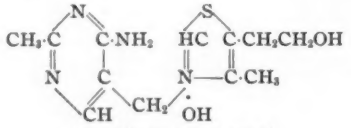
Vitamin B_1 chloride hydrochloride

Vitamin B_1 has the imposing chemical name 2-methyl-5-(4-methyl-5-β-hydroxyethylthiazolium chloride) methyl-6-aminopyrimidine hydrochloride—the formula $C_{12}H_{17}ClN_4OS \cdot HCl$, and a molecular weight of 337.26. It melts at 248–50°C. with decomposition, and is the chloride hydrochloride of a strong base. It occurs as colorless, nearly odorless crystals with a slightly salty taste. It is hygroscopic and very soluble in water, giving a solution acid to litmus which is optically active.

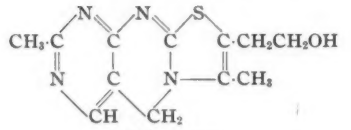
The oxidation of an alkaline solution of vitamin B_1 with potassium ferricyanide gives a yellow basic substance, thiochrome, $C_{12}H_{18}N_4OS$, whose neutral or alkaline solutions are character-

[2] Adsorption is the process by which a substance, often in solution, is condensed or held on the surface of finely divided material, like clay, fuller's earth, etc. It differs in some respects from the process of chemical combination. Elution is the reverse of the process, the liberation of the adsorbed material.

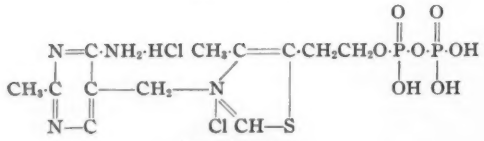
ized by intense blue fluorescence. Phosphorylation of vitamin B_1 produces the pyrophosphate ester, which occurs in yeast as the coenzyme, cocarboxylase.



Vitamin B_1 (Free Base)

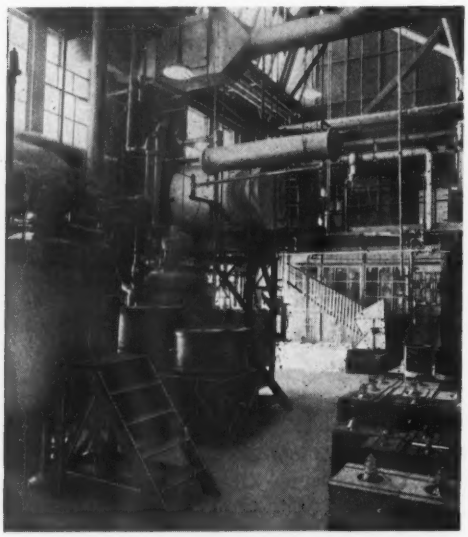


Thiochrome



Cocarboxylase

It has been shown that one of the substances derived from vitamin B_1, called cocarboxylase, is an essential factor in the conversion of glucose in the tissue cells of the animal organism to carbon dioxide and water. In lack of adequate supplies of vitamin B_1, the burning up of the fuel supply to the tissues is incomplete and the full efficiency of the tissue is restricted. As a consequence the nervous tissues can no longer function adequately and the symptoms of vitamin B_1 deficiency develop. These may become manifest by fatigue, loss of appetite, moodiness, fear, and nervousness. Vitamin B_1 is necessary to promote growth in young animals and to maintain growth in adults. It is essential to the maintenance of appetite as an aid to normal digestive functions, and to counteract general malnourishment.



Courtesy of Merck and Co., Inc.

EQUIPMENT USED IN THE MANUFACTURE OF VITAMIN B_1 HYDROCHLORIDE

The chief sources of this vital substance are the whole-grain foods, particularly oatmeal, whole-wheat bread, and other cereal foods. It is also present in milk, potatoes, legumes, and meats such as lean pork, and glandular meats. Unfortunately modern milling processes have lowered the vitamin B_1 content of flour and this source is no longer able to provide the vitamin B_1 necessary for the correct utilization of the carbohydrates, sugar, and starch in the body. It has been estimated that every 100 calories of energy derived from carbohydrates require 10 to 25 international units of vitamin B_1 and, on the basis of 2500 calories per day, the human daily requirement is between 250 and 625 units. Refined sugar has no vitamin content and its use is increasing while the consumption of flour decreases. To offset dietary deficiencies it has been urged that the millers and bakers of the nation start early production of a new flour and bread enriched with vitamin B_1, riboflavin, niacin (nicotinic acid), and iron. Fortunately, the availability of pure vitamins, as a result of commercial production on a synthetic basis, makes it possible to add to the nutrient value of foods without change of their palatability or physical characteristics.

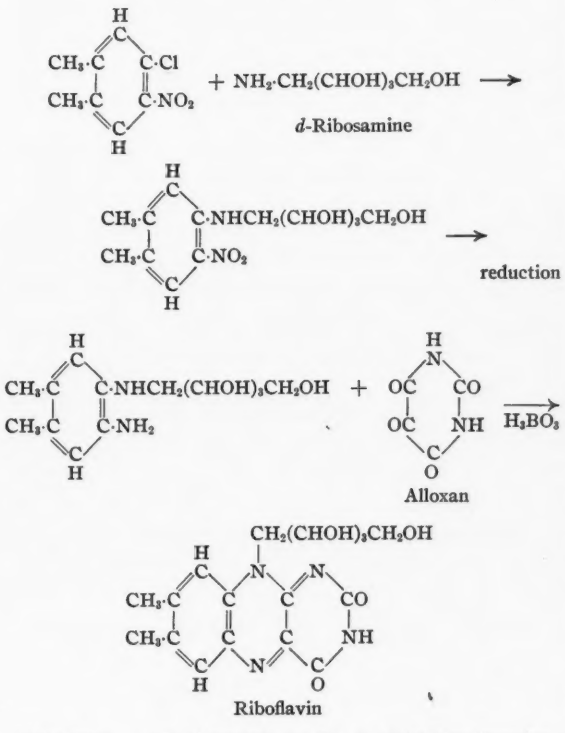
Lacking crystalline vitamin which could be weighed, the biochemist had to devise standards by which the potency of various vitamin B_1 preparations could be measured. These were based on the measurement of the growth of rats or of the time taken to cure symptoms of polyneuritis. Such measurements were expensive, difficult to carry out, and only capable of correct interpretation by highly trained biologists. Various test standards (such as the activity of an International Standard fuller's earth adsorbate) were used. When adequate supplies of synthetic crystalline vitamin B_1 became available the International Commission on Vitamin Standardization unanimously recommended that the international unit for vitamin B_1 be defined as the antineuritic activity of 3.0 micrograms (millionths of a gram) of pure crystalline vitamin B_1 hydrochloride.

In addition to biological methods, the estimation of the vitamin B_1 content of a preparation can also be made by microbiological methods which involve the measurement of the response in growth or of the rate of fermentation of yeasts due to the presence of added vitamin. Recently the use of a chemical method based on the formation and determination of the colored substance, thiochrome, has been intensively studied and is gradually coming into more general use.

Riboflavin.—Riboflavin (lactoflavin, vitamin G, vitamin B_2), a water-soluble, yellow-green, fluorescent pigment of the whey of milk, was known as early as 1879, though its chemical nature remained obscure until 1932 when Warburg and Christian described a "yellow enzyme," obtained from aqueous extracts of yeast, which acts as an oxygen carrier in the cells of all

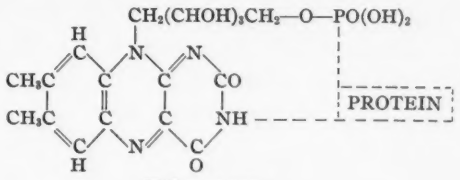
the higher forms of life. In the following year various workers reported the isolation of orange-yellow pigments from a large variety of natural products such as milk, liver, yeast, and egg white. Ellinger and Koschara drew attention to the probable relationship between these pigments and Warburg's "yellow enzyme." Kuhn, attempting to isolate vitamin B_2 from egg white, had obtained a yellow pigment and reported that it had growth-promoting properties for rats, thus linking this and the other pigments with vitamin B_2. Further studies showed the identity of all these pigments.

The pigment riboflavin is extracted with dilute acids and dilute alcohol from the naturally-occurring source material. The acid solution is mixed with fuller's earth and the adsorbed flavin is removed by dilute alcohol containing ammonia or pyridine. The diluted material is concentrated by evaporation, taken up in acetone, and filtered. The flavin is then precipitated as a silver or thallium salt, recrystallized, regenerated as the free flavin, and purified by repeated recrystallizations from dilute alcohol or acetic acid. In this manner Kuhn obtained a tenth of a gram (a five-thousandth of a pound) of riboflavin from the dried egg albumin from 33,000 eggs. From intensive studies of the alkaline hydrolysis of riboflavin and the yellow photo derivative lumiflavin (obtained by exposure of alkaline solutions of riboflavin to light), Kuhn and his co-workers were able to decipher the structural features of riboflavin and, in 1935, to devise a synthesis of riboflavin in which 1,2-dimethyl-4-nitro-5-chlorobenzene was condensed with *d*-ribosamine and the catalytically reduced product was coupled with alloxan in a mixture of acetic and boric acids. Since that time, Karrer and other investigators have published various modifications of the synthesis and so, today, it is possible to prepare pure crystalline riboflavin commercially for nutritional and therapeutic uses.



Riboflavin, 6,7 - dimethyl - 9 - (1′ - *d* - ribityl)isoalloxazine, $C_{17}H_{20}N_4O_6$, molecular weight 376.36, crystallizes from absolute alcohol in clusters of yellow-orange needles, melting at 282° with decomposition. Its solutions exhibit a striking yellow-green fluorescence and are optically active, $[\alpha]_D^{20}$ −110° (in 0.05 *N* NaOH). It is relatively stable to heat but deteriorates on exposure to light.

Theorell has shown that the Warburg yellow respiratory enzyme is a flavin protein which contains riboflavin phosphoric ester (cytoflav) as a prosthetic or active group attached to protein. Kuhn was able to show that the yellow enzyme has the following structure:



Yellow enzyme

That riboflavin is an essential part of one of the enzymes involved in biological oxidations indicates that it is important in cell respiration. It has been suggested that 2 to 3 milligrams of pure riboflavin is the daily human requirement to provide for the needs of the cells and tissues. Riboflavin promotes growth in young animals. In rats its presence tends to prevent dermatitis and loss of hair. In human beings, it is necessary in order to prevent a number of disorders.[3]

Riboflavin is found in such staples as milk, green or leafy vegetables, eggs, liver, kidney, and other meats. It is also present in yeasts. Certain microörganisms used in the commercial production of butanol and acetone by the fermentation of corn starch and molasses form large quantities of riboflavin as metabolic end-products. From the solvent-free residues of these fermentation processes it is possible to prepare various concentrates containing appreciable proportions of riboflavin.

The riboflavin activity of materials is expressed as micrograms of riboflavin per gram of substance. The standard is crystalline riboflavin and the riboflavin content of foodstuffs is determined by its effect upon the growth of rats or bacteria or by ultra-violet fluorescence methods. Although widely distributed in foods, the addition of riboflavin to enriched flour is considered necessary for optimum health.

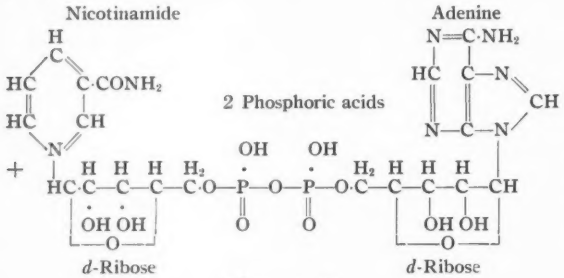
Niacin[4] (*Nicotinic Acid*).—The work of many investigators, particularly that of Goldberger in the United States, demonstrated that the factor necessary for the cure of pellagra was associated with the heat-stable fraction of the vitamin B complex. Dietary treatment with milk, meat, liver, dried yeast, and vegetables cured the characteristic inflammation of the tongue and skin. Following the isolation of riboflavin in 1933 it was shown that deficiency in this factor was not the cause of pellagra. In 1937, Elvehjem demonstrated that

[3] Specifically and technically, ariboflavinosis, a syndrome characterized by cheilosis, a specific type of glossitis, seborrheic follicular keratoses, and corneal vascularization.

[4] The name *niacin* has been suggested as an alternative to nicotinic acid, to prevent confusion with nicotine.

liver extract, known to be very effective in the cure and prevention of pellagra and the related disease of dogs, canine "black-tongue," contained nicotinamide and that black-tongue was cured by nicotinic acid.

The important part that nicotinic acid plays in biochemical oxidations was emphasized two years before its recognition as a pellagra-preventive factor. In 1935, von Euler suggested that nicotinic acid might be part of the respiratory ferment cozymase (coenzyme I). Nicotinic acid amide was also recognized by Warburg and Christian as a hydrolysis product of another (coenzyme II) which they had isolated from horse red blood cells. Coenzyme II contains three phosphoric acid groups but is otherwise similar to coenzyme I which is a complex containing one nicotinamide, one adenine, two pentose, and two phosphoric acid groups:



Coenzyme I

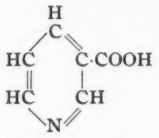
In pellagra and black-tongue the supply of the necessary enzymes in the tissues is depleted and the normal content is restored after treatment with nicotinic acid. These observations indicate that nicotinic acid and

Courtesy of Merck and Co., Inc.

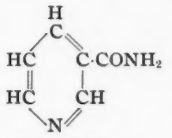
CRUDE OPERATIONS IN THE MANUFACTURE OF NICOTINIC ACID

derivatives, by providing building material for the normal functioning of cells, may thus serve to keep tissue responses normal and healthy. Nicotinic acid is therefore to be regarded not merely as a remedy for a special form of skin disease but as an agent to keep tissue metabolism normal, just as B_1 is considered essential to normal nerve metabolism in prevention of polyneuritis.

Nicotinic acid, 3-pyridine carboxylic acid, $C_6H_5NO_2$, molecular weight 123.11, melting at 235–7°, is a white, odorless, crystalline powder which sublimes on heating. It was first prepared synthetically by Hüber in 1867 by the oxidation of the alkaloid, nicotine, with nitric acid. It is soluble in water, alcohol, and warm glycerol, but insoluble in ether. It forms salts with dilute alkalies and alkaline earths and with mineral acids. Its amide also has antipellagric activity.



Nicotinic acid



Nicotinamide

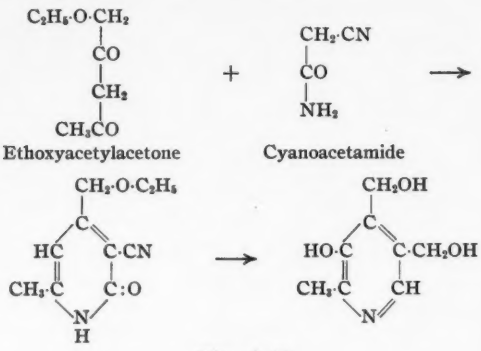
Nicotinic acid in foodstuffs can be determined by dog black-tongue curative tests using crystalline nicotinic acid as a standard; by chemical estimations depending on the fact that nicotinic acid reacts with cyanogen bromide to give a yellow color, the intensity of which is increased three- to fivefold by the addition of aniline; and by microbiological methods involving response in growth of bacteria.

Although some symptoms of pellagra may be cured by nicotinic acid it is unusual to find an undernourished subject with only one vitamin B deficiency, since a deficient diet is generally insufficient in each and all of the members of the B complex.

Vitamin B_6.—During the course of Goldberger's work on the pellagra-preventing factor, he was able to produce a group of diseases in rats fed on diets deficient in the pellagra-preventing factor. This so-called "rat pellagra" was shown, in 1935, by György to be due to a deficiency of a separate unique factor which he designated as vitamin B_6.

In 1938, the crystalline vitamin was isolated from rice bran by Keresztesy and Stevens in the Merck Research Laboratories, and shortly afterward the same isolation was successfully accomplished by Kuhn, György, Lepkovsky, and others.

Studies of the chemical and physical properties of the crystalline vitamin enabled other investigators to determine the structure of the vitamin and later to accomplish its synthesis successfully, starting with ethoxyacetylacetone and cyanoacetamide.

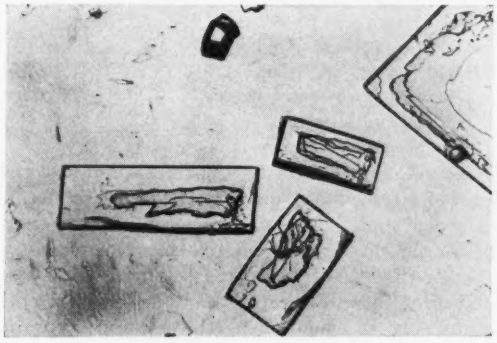


Ethoxyacetylacetone

Cyanoacetamide

Vitamin B_6

Vitamin B_6, pyridoxine (adermin), 2-methyl-3-hydroxy-4,5-bis-(hydroxymethyl)pyridine, $C_8H_{11}NO_3$, molecular weight 168.17, forms white platelets of a hydrochloric acid salt, melting point 204–6°.



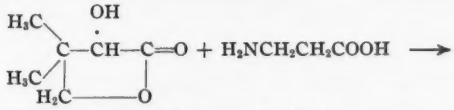
Courtesy of Merck and Co., Inc.

PHOTOMICROGRAPH OF CRYSTALLINE VITAMIN B_6

Pyridoxine (the chemical name for vitamin B_6), occurs in seeds of cereal grains and legumes, yeast, meats, and fish. The unit of pyridoxine is the minimum amount which will cure a certain type of skin disease[5] in suitably standardized rats in 21 days. Attempts have been made to assay vitamin B_6 by its influence on the growth and on acid formation by the bacterium *Streptobact. plantarum*. Chemical methods have also been developed for the determination of pyridoxine by color reactions. In human beings cured of pellagra and beriberi, but still living on deficient diets, it has been reported to have relieved extreme nervousness, insomnia, abdominal pain, and difficulty in walking.

Pantothenic Acid.—In 1933, Roger J. Williams and his co-workers at Oregon State College showed that extracts of very diverse tissue contain material capable of stimulating the growth of yeast, and in 1938 they were able to isolate the material, pantothenic acid (from the Greek, signifying "from everywhere"), in the form of its impure calcium salt. Another principle from the vitamin B complex, known as the "chick antidermatitis factor," was shown to be equivalent in its biological effects to pantothenic acid. In 1940 it was possible to announce the structure and synthesis of physiologically active pantothenic acid, fully identical in all chemical, physical, and physiologic properties with the naturally occurring vitamin universally present in all biologic tissues.

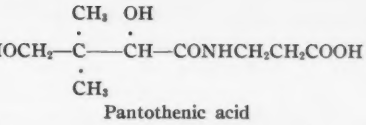
The synthesis involved the condensation of a lactone with the well-known cleavage product, β-alanine:



α-Hydroxy-β,β-dimethyl-γ-butyrolactone

β-Alanine

[5] Acrodynia.

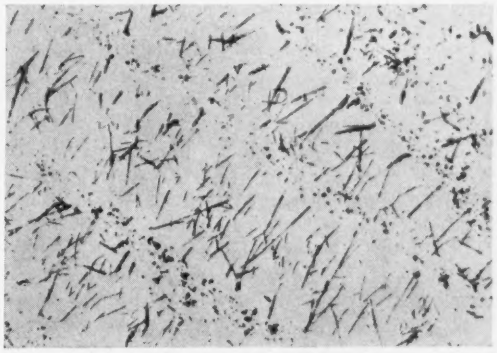


Pantothenic acid

Pantothenic acid, N-(α,γ-dihydroxy-β,β-dimethylbutyryl)-β-aminopropionic acid, $C_9H_{17}NO_5$, molecular weight 219.23, has been isolated as a pale yellow viscous oil which is dextrorotatory, $[\alpha]_D^{25}$ + 37.5°. It forms a microcrystalline calcium salt, $[\alpha]_D^{26}$ + 24.3°. The assay of pantothenic acid is based either on chick growth determinations or on microbiological estimations involving the growth response and lactic acid production by *Lactobacillus casei*.

It is present in milk and in all tissues, of which liver is the richest source. It would seem that it is an essential factor in tissue respiration and its universal presence is explained on this basis.

As with thiamine, riboflavin, niacin, pyridoxine, and ascorbic acid, the isolation and the determination of the structure of pantothenic acid have been rapidly followed by a laboratory synthesis and a reduction of this purely academic achievement to commercial practice. Thus, once again, a rare physiologic factor, obtainable only by the labor of love of a group of devoted enthusiasts, at enormous cost of time and material, and then only in amounts totally inadequate for general use, has been made readily accessible to the nutritional and clinical investigator, with the ultimate plan of its commercial supply to the recognized sources in the food and medicinal fields. With the aid of such pure, crystallized, commercially available vitamins the investigator can rapidly clear away the clouds that dim the brightness of our knowledge in the nutritional fields, and the doctor has material support in his attack on



Courtesy of Merck and Co., Inc.

PHOTOMICROGRAPH OF CRYSTALS OF PANTOTHENIC ACID

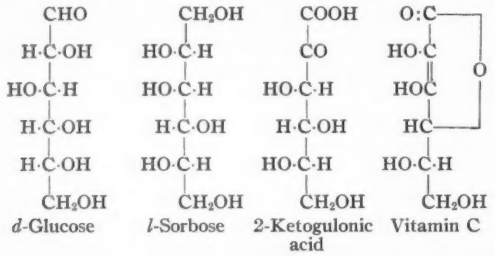
the many deficiency diseases, with their various manifestations, that afflict suffering mankind.

Vitamin C (Ascorbic Acid)

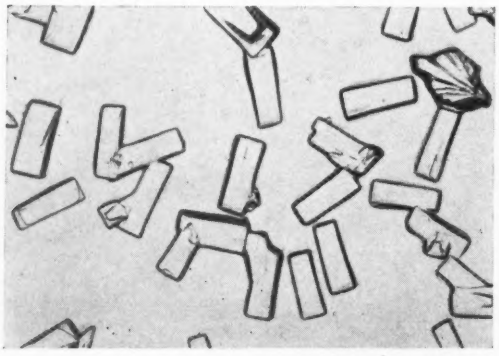
The observation of Holst and Frölich in 1907, that the guinea pig could be used as an experimental animal in scurvy, made it possible to measure "antiscorbutic" activity in a satisfactory and quantitative manner,

but attempts to isolate the vitamin from natural products encountered great difficulty because of its extreme sensitiveness to destruction by oxidation. The isolation of the vitamin from lemons as "hexuronic acid" by Waugh and King in 1932 was followed by confirmation by workers in many other laboratories, and Szent-Gyorgyi was able to prepare quantities from adrenal glands and from paprika. With this material the structural formula of the vitamin was established in 1933 and methods of synthesis were devised.

A method which has great commercial significance is based on the use of sorbitol, produced by the reduction of *d*-glucose on a commercial scale. The sorbitol is oxidized by selective fermentation to the sugar, *l*-sorbose, and is readily converted by oxidation to 2-ketogulonic acid, which lactonizes and enolizes in an acid medium to form vitamin C.

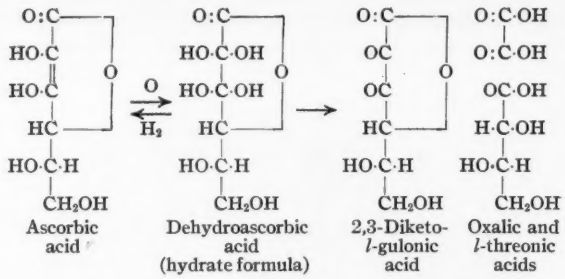


Vitamin C (ascorbic acid), 2,3-dienol-gulonic acid lactone, $C_6H_8O_6$, molecular weight 176.06, is a white, odorless, crystalline powder which melts at 189–92°. It is freely soluble in water and is soluble in alcohol and in glycerol. It is a comparatively strong organic acid; the acidity of aqueous solutions ranges from pH 3 to pH 2 for concentrations increasing from 5 to 50 mg. per cc. The physiologically active *l*-ascorbic acid is the levo modification with specific rotation $[\alpha]_D^{25}$ 21.0°. In the dry state the acid is reasonably stable to exposure but it rapidly oxidizes in aqueous solutions. The oxidation, which is accelerated in the presence of alkalies and by traces of metals, takes place by a first reversible oxidation stage to physiologically active dehydroascorbic acid. This may be reduced to ascorbic acid, may change into the physiologically inactive 2,3-diketo-*l*-gulonic acid, and may be irreversibly oxidized to *l*-threonic acid, oxalic acid, and carbon dioxide.



Courtesy of Merck and Co., Inc.

PHOTOMICROGRAPH OF CRYSTALLINE VITAMIN C



Vitamin C is essential to the formation and maintenance of intercellular substances of teeth, bones, and the blood system. It has been accepted as a specific agent for the prevention and treatment of scurvy. It is possible that the vitamin plays a more specific role in relation to infectious processes than any of the other vitamins. It is essential to the healing of wounds and may play a vital part in the maintenance of a healthy condition of the teeth and gums.

The outstanding dietary sources of vitamin C are fresh fruits and vegetables, particularly citrus fruits and the succulent or leafy vegetables. Although the citrus fruits are best known as sources for the vitamin, many other fruits constitute rich dietary sources of this accessory food factor, notably strawberries, currants, gooseberries, and raspberries. Green vegetables such as cabbage, broccoli, spinach, and watercress also provide liberal proportions of the vitamin as do potatoes, turnips, and tomatoes. The international unit is the activity possessed by 0.05 milligram of crystalline ascorbic acid.

The content of the vitamin in foodstuffs, and in preparations and biological material, can be estimated by guinea-pig scorbutic hemorrhage prevention, or by guinea-pig tooth development tests, but the majority of determinations are made by colorimetric chemical tests which depend on the use of dyes which are readily decolorized in the presence of a reducing substance such as vitamin C. The most commonly employed indicator is Tillman's reagent, the well-known oxidation-reduction dyestuff, 2,6-dichloroindophenol.

The ready availability of commercial ascorbic acid and the development of accurate chemical methods of determination have given great impetus to the study of the compound's activity within the human body, which has resulted in the immeasurable expansion of our knowledge of the physiologic action of vitamin C, of the changes resulting from its deficiency, and of human requirements for the vitamin and the factors which affect them. The average daily requirement has been estimated as 300–500 international units daily for infants and 800–1200 international units for adults. These requirements are increased during pregnancy and lactation.

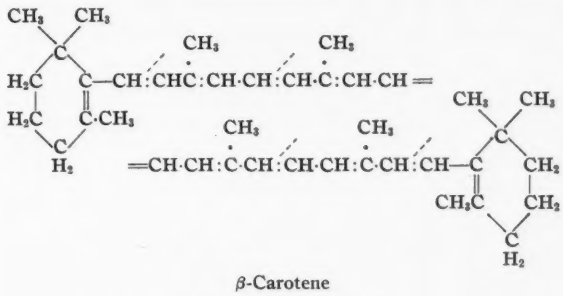
THE FAT-SOLUBLE VITAMINS

The "unidentified dietary factor, fat-soluble A," discovered in 1913 by McCollum and Davis in butter, was shown to occur also in various oils. In 1922, McCollum and his co-workers reported experiments on the po-

tency of different oils in the cure of the eye disease, xerophthalmia. They also determined the values of the same oils in promoting growth of young rats on calcium-deficient diets, and in inducing deposition of calcium salts in bones. They came to the conclusion that the power of certain fats to promote the cure of the bone disease, rickets, depends on the presence of a fourth vitamin, called vitamin D, since the vitamins A, B, and C had already been postulated. This vitamin is distinct from fat-soluble A (vitamin A), since it will neither prevent nor cure xerophthalmia. By a series of very extensive and carefully planned experiments, Steenbock and Nelson in 1923 were able to confirm this finding that vitamins A and D are distinct entities. To these fat-soluble vitamins, later workers added the antisterility vitamin E and the coagulation vitamin K.

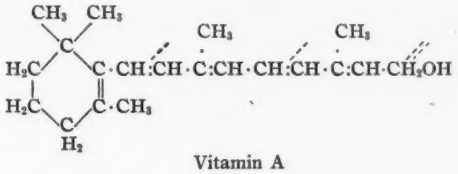
Vitamin A

The brilliant researches of Karrer and his associates, which established in 1930 the chemical constitution of the yellow-red plant pigment carotene and of vitamin A from fish oils, served to establish the chemical basis for the conversion of carotene to vitamin A in the body.

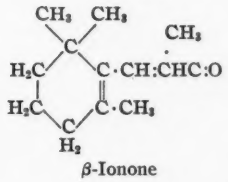


β-Carotene

The aliphatic central chain of β-carotene may be regarded as a series of four dehydrogenated isoprene (β-methylbutadiene) residues arranged in a double pair united by a central double bond capable of hydrolysis, thus giving rise to an alcoholic group in each of the split products. Consequently, β-carotene, which contains two β-ionone rings, can cleave to give two molecules of vitamin A.



Vitamin A



β-Ionone

Of the thirty or more carotenoids whose chemical structure is now well established only four have the β-ionone ring and these, α-carotene, β-carotene, γ-carotene, and cryptoxanthin, are the only ones which are converted in the body into vitamin A.

Carotene, pro-vitamin A, $C_{40}H_{56}$, molecular weight 536.85, occurs in green leafy and yellow vegetables as a mixture of the three isomeric modifications: α-, melting at 183°, $[\alpha]_{6}^{18}$ +385° (in benzene); β-, melting point 187°; and γ-form, melting point 178°. It forms dark red, lustrous crystals which oxidize rapidly on exposure. It is soluble in chloroform, benzene, and in oils. With antimony trichloride in chloroform it gives a blue solution.

Vitamin A, the antixerophthalmic vitamin, $C_{20}H_{29}OH$, molecular weight 286.44, probably occurs in two or more forms with slight intramolecular variations. It is a pale yellow, viscous liquid, boiling at 137–8° at 10^{-6} mm., which forms pale yellow crystals melting at 7.5–8.0°. It is fat-soluble and gradually decomposes on exposure to atmospheric oxidation.

In human nutrition a considerable part of the vitamin A activity is supplied by carotene from vegetables. Eggs, milk, and butter are the usual sources of vitamin A and these are supplemented by vitamin A obtained from fish oils in which the fish stores up vitamin A derived from its own food.

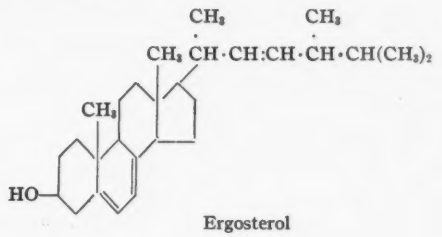
Methods of estimation of vitamin A in foodstuffs are chemical, using a tintometer which measures the intensity of blue color developed by anhydrous antimony trichloride solution in chloroform; physical, based on the ability of vitamin A to absorb ultraviolet light of a wave length of 3280 Angström units; and biological, involving the growth of white rats.

The international unit is the activity possessed by 0.6 microgram of pure β-carotene. Standard cod-liver oil, as specified by the U. S. Pharmacopoeia, contains 3000 international units per gram.

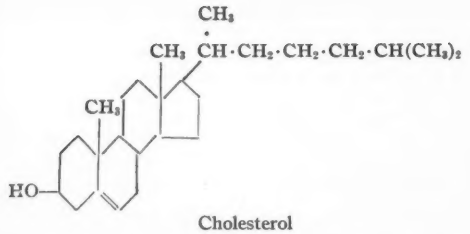
Evidence for the existence of vitamin A and its role in nutrition is based on the fact that a characteristic eye disease, usually called xerophthalmia, results from a deficiency in this vitamin. It also helps to maintain high visual acuteness and is specific for the type of "night-blindness" called nyctalopia. It is necessary for normal growth and helps to maintain the health of the tissues of the respiratory tract. It is generally agreed that the average adult needs at least 4000 international units of vitamin A per day.

Vitamin D

In 1879, Tanret isolated a sterol from ergot to which he gave the name ergosterol. The sterols are an important group of compounds which occur in practically all animal and plant tissues and their derivatives include not only vitamin D but such biologically important substances as the bile acids, cardiac glycosides, toad poisons, and sex hormones. The group has a general structural formula, which is capable of almost infinite modification.

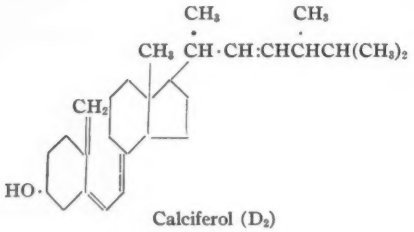


Ergosterol

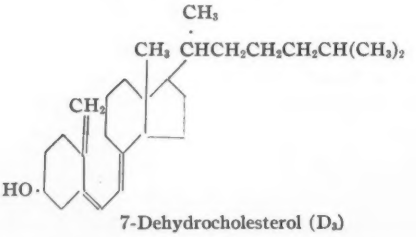


Cholesterol

The irradiation of ergosterol with ultra-violet light was discovered by Hess and Steenbock to produce vitamin D (calciferol) and it was soon found that the change could also be brought about by bombardment with cathode rays. With this discovery the relation of sunlight to rickets was clarified, because it was evident that the human skin contains "pro-vitamin" sterols which are activated by the ultra-violet rays of sunshine to form vitamin D, which is absorbed and utilized by the body. In 1934, Waddell, studying the treatment of rickets in chicks, found that the vitamin D in cod-liver oil was more potent for chicks than calciferol. The search for another form of vitamin D resulted in the discovery of vitamin D_3, (7-dehydrocholesterol).



Calciferol (D_2)



7-Dehydrocholesterol (D_3)

The irradiation of ergosterol gives rise to a series of compounds: lumisterol, tachysterol, calciferol, toxisterol, and suprasterol. An addition compound of lumisterol and calciferol is extremely stable and was formerly classed as vitamin D_1.

Vitamin D_2, calciferol, $C_{28}H_{44}O$, molecular weight 396.63, is obtained as white, odorless crystals, melting at 115–17°, from the irradiation or bombardment of ergosterol. The sterol is insoluble in water; soluble in alcohol, ether, chloroform, acetone, and vegetable or fish oils. It is optically active and has a specific rotation of $[\alpha]_D^{20}$ 102–5° in absolute alcohol.

Vitamin D_3, 7-dehydrocholesterol, the natural antirachitic vitamin of fish oils, milk, butter, and eggs, $C_{27}H_{44}O$, molecular weight 384.45, occurs as colorless crystals melting at 82–4° and is optically active, $[\alpha]_D^{20}$ 83.3° in acetone.

Vitamin D was discovered in the search for a factor preventive of rickets and to date its principal function has been its use as an "antirachitic" agent. It acts by controlling the proper metabolism of the mineral elements calcium and phosphorus in bone formation, and is essential for the prevention of infantile rickets, and certain other conditions in both infants and adults.[6] It is needed for the building and maintenance of strong bones and teeth.

It is tested for in foodstuffs and pharmaceutical preparations by the rat curative "line test" based on recalcification resulting from 7 or 10 days feeding of test material to standardized depleted rats. Interpretation is based on calcification of sectioned wrist bone as revealed by staining with silver nitrate.

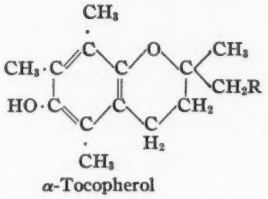
The international unit is the vitamin D activity of 0.025 microgram of crystalline vitamin D_2. In other words, crystalline calciferol has a potency of 40,000 international units per gram. Vitamin D_3 has the same antirachitic potency as calciferol.

Vitamin E (α-Tocopherol)

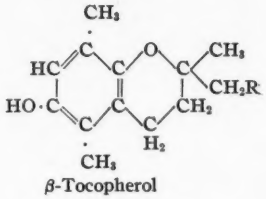
In 1922, Evans and Bishop first succeeded in proving the existence of a vitamin factor vital to reproduction which they found in wheat-germ, cottonseed, lettuce, and a variety of other vegetable oils. In rats, kept on a diet free from this so-called vitamin E, sterility resulted after a more or less extended period. Mating occurred normally, but pregnancy invariably terminated in fetal death followed by resorption.

All common methods for the isolation of the active principle in pure form were unavailing until Evans, Emerson, and Emerson in 1936 treated the non-saponifiable fraction of wheat-germ oil with cyanic acid and succeeded in isolating the crystalline allophanates of α- and β-tocopherol (*tokos*, childbirth; *phero*, to bear; *ol*, alcohol). Soon thereafter they isolated this same α-tocopherol together with another active substance, γ-tocopherol, from cottonseed oil. These tocopherols have varying physiological activity and it is evident that one may speak of the multiple nature of vitamin E in the same sense as one accepts the fact that there are several substances with vitamin A and vitamin D activity.

In 1937, the late Erhard Fernholz in the Merck Research Laboratories thermally decomposed α-tocopherol to give tetramethylhydroquinone, identical with a pure sample of material furnished by Lee I. Smith of the University of Minnesota. Further work on the oxidation of α-tocopherol with chromic acid enabled Fernholz to assign the correct structure to the compound. Later, other workers confirmed this finding and it was shown that the α-, β-, and γ-tocopherols were closely related compounds. The road was thereby opened for the devising of methods of synthesis of vitamin E on a commercial scale by the condensation of the hydroquinone with phytol [$HOCH_2CH{=}C(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_3C(CH_3){=}CH_2$, the alcoholic constituent of chlorophyll], the phytyl halides, or with phytadiene.

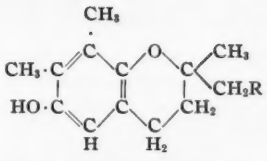


α-Tocopherol



β-Tocopherol

[6] Specifically and technically, spasmophilia or infantile tetany, and osteomalacia in adults.



γ-Tocopherol

(where R = $CH_2CH_2CHCH_2CH_2CH_2CHCH_2CH_2CH_2CHCH_3$)

Alpha-tocopherol, the antisterility vitamin, $C_{29}H_{50}O_2$, molecular weight 430.69, is a colorless or slightly yellow, odorless oil. It is stable to heat but impaired by association with rancid fats. It reduces alcoholic silver nitrate.

It is of value in preventing nutritional sterility in rats and it has been reported to be of value in the nutrition of other animals.

The content of vitamin E in foodstuffs and pharmaceutical preparations is estimated by the use of standardized female rats to measure the minimum amount of test material which will ensure fertility. In addition to the biological methods for the assay of the vitamin, physical and chemical assays by measurement of absorption; electrometric titration with gold chloride; colorimetric estimation with dipyridyl of the ferrous iron resulting from the oxidation of vitamin E with ferric chloride; and measurement of the red color produced on heating with alcoholic nitric acid, have been suggested.

Although, at the present time, there does not exist sufficient evidence to indicate the extent of the deficiency of the vitamin in the diet or to support completely claims for benefits to be derived from its use, the isolation and synthesis of the pure compound have made possible the elaboration of chemical assay methods, the estimation of its distribution in foodstuffs, and the initiation of physiological and clinical studies to remedy the deficiencies in our present knowledge.

Vitamin K

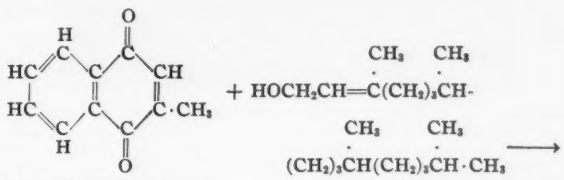
From 1929 onward various investigators had reported a bleeding tendency in chicks reared on artificial diets, but it was not until 1935 that Henrik Dam and Fritz Schønheyder at the Biochemical Institute of the University of Copenhagen reported that the deficiency factor responsible for the hemorrhage in the chicks was a fat-soluble substance occurring in hog liver, hempseed, cereals, and vegetables. This factor was shown to be different in nature from the oil-soluble vitamins A, D, and E, and Dam designated it vitamin K (Koagulations-Vitamin).

The bleeding tendency in the chicks was found by Schønheyder to be associated with a decrease in the concentration of prothrombin in the plasma. In the same year, Almquist and Stokstad showed that the antihemorrhagic factor was localized in the nonsaponifiable fraction of alfalfa lipids, that chlorophyll and sterol fractions from the alfalfa were impotent and that neither carotene nor xanthophyll was effective as an antihemorrhagic agent.

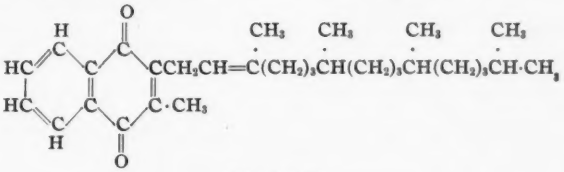
Green leafy tissue is perhaps the richest natural source of the plant form of the vitamin. As little as one-half per cent of commercial dried alfalfa in the diet of the chick will meet the normal requirements. Following early observations on the development of marked "antihemorrhagic" activity in foodstuffs during bacterial spoilage it was found that certain bacteria synthesize and retain a fat-soluble antihemorrhagic substance. Concentrates with vitamin K activity were first made by extracting dried alfalfa with hexane or by the petroleum ether extraction of putrefied fish meal or rice bran.

Extensive investigation of the chemical aspects of vitamin K soon brought about the isolation and synthesis. In May, 1939, Doisy and his associates in St. Louis reported the isolation of vitamin K_1 as a light yellow oil from alfalfa and vitamin K_2 as a light yellow, crystalline solid from putrefied sardine meal.

A few months later these workers reported on the synthesis and, independently, Fieser and his co-workers were able to show that heating phytol with a large excess of 2-methyl-1,4-naphthoquinone in dioxane gave synthetic vitamin K_1, which was proved by the Merck Institute for Therapeutic Research to have marked antihemorrhagic activity, apparently identical with that of vitamin K_1 from natural sources.



Methylnaphthoquinone Phytol



Vitamin K_1

From results obtained in the Squibb and Merck Research Laboratories it would appear that the simple compound, 2-methylnaphthoquinone, possesses antihemorrhagic activity of the same order of magnitude as vitamin K_1 and it has been suggested that it be adopted as a standard for assay so that the unit of vitamin K activity could be defined as that of one microgram of pure 2-methyl-1,4-naphthoquinone. It has been shown that many compounds closely related to this simple substance have vitamin K activity.

2-Methyl-1,4-naphthoquinone, $C_{11}H_8O_2$, molecular weight 172.17, melting point 104–6°, occurs as yellow crystals slightly soluble in water. Vitamin K_1, 2-methyl-3-phytyl-1,4-naphthoquinone, $C_{31}H_{46}O_2$, molecular weight 450.67, is a golden-yellow, mobile oil, distilling at 140–5°C. at 10^{-5} mm. It is completely soluble in ether and petroleum ether but insoluble in water. The assay of foodstuffs for vitamin K_1 is carried out by a chick assay method in which the effective dose of vitamin K_1 is about 1.0 to 1.5 micrograms per chick. The activity of 2-methyl-1,4-naphthoquinone and the ease with which it lends itself to modification to produce phosphoric and other esters which are water-soluble and useful in therapy provide medicine with economical and large scale supplies of material with vitamin K activity.

Vitamin K active substances aid in the clotting of blood and the prevention of some forms of hemorrhage.

The vitamin is essential to the formation of the substance prothrombin, necessary to the clotting of blood.

Courtesy of Merck and Co., Inc.

CHEMICAL ASSAY FOR VITAMIN K

OTHER VITAMINS

Besides choline, inositol, *p*-aminobenzoic acid, and biotin, and the as yet unisolated and unidentified factors of the B complex, various other vitamins have been postulated, including vitamin I (Centanni's digestive factor), vitamin J (Von Euler's pneumonia factor), vitamins L and L_2 (lactation factors), vitamin M (monkey-pellagra factor), vitamin P (citrin), vitamin U (chick-growth factor), and vitamin W (rat-growth factor), together with others still without alphabetical designation.

The work goes on comparatively rapidly, since the whole of our knowledge of the chemistry of the vitamins has been acquired in the last thirty years. Today, every mother knows the value of orange and tomato juice in the feeding of her baby to prevent infantile scurvy; and of the use of cod-liver and other oils, together with sunshine, in the bringing up of strong, vigorous, long-boned children. At the present time, the governments of the various nations recognize the value of vitamin B_1 as a "morale" vitamin for soldier and civilian alike, and are taking steps to enrich foodstuffs with vitamins and minerals. The yoke of the deficiency diseases has been partially lifted from the neck of the human race and future progress in vitamin chemistry and nutritional knowledge will further lighten the burden and advance the happiness and welfare of mankind.

A SIMPLE SODIUM PRESS FOR THE SMALL LABORATORY

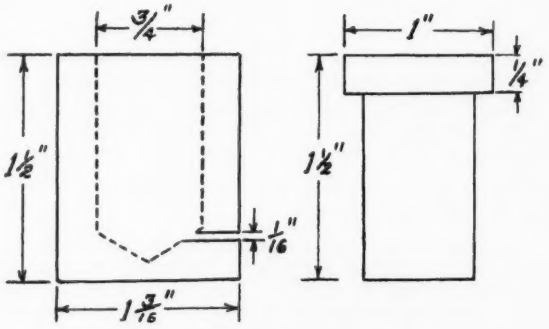
WALTER C. BEARD, JR.

Rollins College, Winter Park, Florida

THIS sodium press was designed for use in small laboratories where the demand for sodium metal in the wire form is not sufficient to warrant the purchase of a standard press. It was made with the following thought in mind: simplicity of construction, in order that there might be as few parts as possible, requiring a minimum of machine work. The press consists essentially of a simple piston and cylinder arrangement with a small hole in the cylinder through which the sodium is forced in the form of a wire. Strictly speaking this is not a "press" itself but rather a device to be used in some convenient pressing mechanism such as a vise or similar machine.

The metal used was scrap cold-rolled steel shafting. The original dimensions are given in the figure; however, any variation to suit material at hand would serve as well. The piston should fit rather loosely to facilitate removal. The cylinder was bored with an ordinary machine bit and then dressed out with a boring bar; then the piston was made to fit. The size of the extrusion hole depends upon the size of wire desired. Too small a hole is not desirable.

This press will contain four grams of sodium giving 223 centimeters of wire at this particular bore. The press should be operated in such a manner that the extrusion hole is away from the operator to prevent the danger of the sodium's being "shot" into the face. As the wire emerges it should be caught in kerosene or paraffin oil.



SODIUM PRESS

The Old Tungsten Mine at Long Hill, Connecticut[1]

FREDERICK H. GETMAN[2]

Hillside Laboratory, Stamford, Connecticut

THE existence of a unique deposit of tungsten ore in the vicinity of the village of Trumbull, Connecticut, has been known to geologists since the early part of the last century. As early as 1837 C. U. Shepard (*1*) called attention to this deposit in these words:

"This is another of the rare metals not hitherto applied to any use, except on a small scale as a yellow pigment in the state of tungstic acid. Still its presence is everywhere viewed with interest as being indicative of the metal tin."

He further pointed out that the "*sole* repository of the prismatic barite ore of tungsten in the United States occurs at Trumbull" and suggested that "this deposit offers an invitation to scientific research."

This interesting source of tungsten was discovered near the village of Trumbull on a rounded knoll known as Long, or Skagnewamp Hill, about two hundred feet above the bed of the Pequonnock River. It is one of those typical contact ore deposits so abundant throughout the western part of Connecticut and was found to occur at the surface of contact between limestone and gneiss in the neighborhood of one or more pegmatic dikes. According to Schairer (*2*)

"A bed of crystalline limestone occurs between two layers of hornblende-gneiss. The formations are cut by pegmatites which supplied the ore solutions with fluorine, boron and tungsten. The rich ore was found at the contact between the limestone and the lower layer of hornblende-gneiss. The gneiss contains hornblende, feldspar, biotite, titanite, ilmenite, pyrite and apatite."

Although the announcement of the discovery of tungsten ore at Long Hill was received with interest by mineralogists, it was not until some years later that the deposit was exploited industrially. Even after mineralogists had recognized this as a source of rare specimens of pseudomorphs resulting from the transformation of the original scheelite, or calcium tungstate, into wolframite, or tungstate of iron and manganese, the prosaic miner merely confined his attention to the removal of the small amounts of the ores of silver, copper, and lead which were coexistent with the tungsten. At a later date, before the mining of tungsten ore was undertaken, limestone was quarried and converted into lime, while still later certain of the pegmatite veins were worked by the porcelain industry.

The exploitation of the valuable tungsten minerals was not commenced until 1898, when the Rare Minerals Company undertook systematic mining operations. Later on the property was acquired by the American Tungsten Mining and Milling Company which continued operation of the mine until the best of the ore was practically exhausted.

The first scientific exploration of the Long Hill deposit of tungsten was made by Adolph Gurlt of the University of Bonn in 1887 (*3*). In his report he wrote:

"The gneiss encloses a bed of crystalline limestone 35 to 45 feet thick, exposed over an area of about 25 acres, and only covered by gneiss in South Hill, near the southern boundary of the property where copper, lead and silver mining had been carried on. . . .The wolfram (tungsten) ore consisting of wolframite, scheelite and wolfram-ochre, occurs upon a so-called contact deposit of 3 to 5 feet which is embedded between the crystalline limestone and the lower gneiss."

Subsequent to the foregoing study by Gurlt, a survey of the tungsten mine at Long Hill was conducted by Hobbs (*4*). The geological map shown in Figure 1

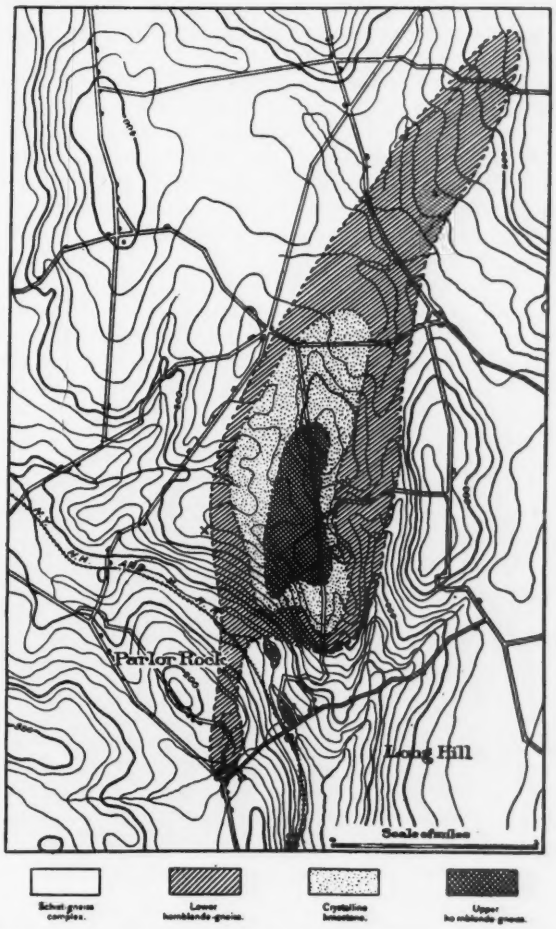


FIGURE 1.—GEOLOGICAL MAP OF THE VICINITY OF THE TRUMBULL MINE

[1] Presented before the Division of the History of Chemistry at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 9, 1941.

[2] Notice of Dr. Getman's death appeared in J. CHEM. EDUC., **19**, 26 (1942).

is reproduced from Hobbs' account of the mine and clearly indicates the relative positions of the strata of hornblende-gneiss and limestone. The tracks of the New York, New Haven, and Hartford Railroad as shown on the map have been torn up since this survey was completed in 1900. In referring to the contact zones between the hornblende-gneiss and the limestone, Hobbs writes:

"Especial interest attaches to these zones... because of the marked changes in the rocks near these contacts, the exceptional nature of the included minerals and their alteration products, and because here is found the tungsten ore. Essentially the same minerals are found at the two limestone contacts, though the tungsten minerals, scheelite and wolframite, are generally more abundant at the lower contact surface... As regards the distribution of the tungsten minerals no law can be laid down, save the one that the ore is concentrated just below the lower contact, with the widest variations as regards its lateral concentration."

In connection with the discussion of the crystal form of the mineral scheelite, as found at the Long Hill mine, Hobbs points out that the distorted crystals and aggregates of wolframite were as a rule spongy in texture and partially composed of scheelite, the two minerals having formed a network in which the wolframite penetrated the scheelite. Furthermore, the process of alteration from scheelite to wolframite apparently had proceeded further, since rusty masses of material were found associated with wolframite in which pseudomorphs of limonite and wolframite occurred after scheelite, indicating that the process of introducing iron into the scheelite probably has commenced with replacement of calcium and terminated with the complete expulsion of tungsten.

The two companies which operated the Long Hill mine for tungsten ore enjoyed a relatively brief period of activity. The mine was opened in 1898, and after three years of intensive operation the yield of ore became so small as to render further mining an unprofitable undertaking. Few statistics are available concerning the yield of ore during the three years of active

FIGURE 2

mining but apparently not much more than a few tons of pure scheelite were obtained during this brief period. Over $60,000 were expended in the erection of suitable buildings and the installation of the necessary machinery in the exploitation of this deposit of tungsten ore. Thus, while the importance of the discovery of tungsten in Connecticut is unquestioned, the exploitation of the ore as a commercial venture proved to be unprofitable.

Despite its relatively brief history, however, an outline of the process of mining carried out at Long Hill should be given. The upper bed of hornblende-gneiss, where it appeared at the summit of the hill, was removed and a pit was sunk to facilitate the removal of the scheelite-bearing rock. The larger masses of rock, after removal by blasting, were broken by sledges and the selected material transported to the crushing-mill by bucket-conveyor. This mill was erected near the southwestern base of the hill as indicated in Figure 1 and was furnished with an appropriate siding from the adjacent railroad tracks. The machinery of the mill consisted of a crusher having a capacity of 10 tons per hour which discharged its product onto a "picking-table," an endless belt of rubber serving as a carrier and feeder to two smaller crushers on the floor below. The latter delivered their output, in turn, to two sets of rolls running one-fourth inch apart. The material discharged from these rolls was then raised by means of an endless belt to the top of the mill where it was delivered to a revolving screen having meshes one-eighth inch square. Here much of the accumulated dust was removed by means of a current of air injected below the screens. The coarser material rejected by the screens was carried by gravity to another pair of rolls running one-eighth inch apart. The material leaving these rolls was returned to the elevator and again allowed to pass through the screens. After having been screened a second time it was subjected to further screening in gyrating sieves of three successive grades of fineness. The final concentration was effected in a pneumatic concentrating machine which delivered the concentrate clean and with relatively little concentrate in the tailings. The scheelite, as finally delivered from the mill, contained a small amount of pyrite as an impurity, but this was subsequently removed by roasting. Separation of the calcium and ultimate conversion of the material into tungstic oxide was not undertaken at the mine. The crushing machinery was driven by a 200-horsepower, high-speed engine, while an engine of smaller size was employed to drive the concentrating machinery. Upon the cessation of mining operations, the machinery was sold and the mill torn down. Today the visitor to the site of the former tungsten mine can readily detect the outlines of the mill and, at various points on the hill, can discover a number of test shafts (Figure 2) which apparently were sunk in the hope of finding fresh deposits of tungsten ore.

It is worthy of mention that fluorite is one of the most abundant among the numerous minerals found in association with those of tungsten at Long Hill. This is not surprising since the intruding pegmatites which are believed to have supplied the ore solutions with tungsten might also be expected to furnish fluorine and boron as well.

Much of the fluorite occurring here is of the form known as chlorophane, a mineral which glows with a beautiful greenish phosphorescence when heated in the flame of a Bunsen burner. In fact, Long Hill is one of the few localities where this interesting form of fluorite is to be found in abundance in the United States.

Another mineral found here is titanite in characteristic thin, wedge-shaped crystals, containing approximately 30 per cent of titanium.

Notwithstanding the fact that the abandoned tungsten mine at Long Hill has ceased to possess interest as a possible source of tungsten, it yet continues to engage the attention of both mineralogists and scientific historians.

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(1) SHEPARD, "A report on the geological survey of Connecticut," published by the State, New Haven, 1837.
(2) SCHAIRER, "The minerals of Connecticut," published by the State, Hartford, 1931.
(3) GURLT, *Trans. Am. Inst. Mining Engrs.*, **22**, 236 (1894).
(4) HOBBS, *U. S. Geol. Survey*, 22nd Ann. Report, **2**, 7 (1901).

APPARATUS FOR SEMIMICRO FILTRATION[1]

JACOB CORNOG and FLOYD O. KRAUSE

The State University of Iowa, Iowa City, Iowa

A NUMBER of methods have been suggested for separating precipitates from filtrates on a semimicro scale. This paper reports some of them that have been tried by the authors. Much of the apparatus is unavailable on the market and must be improvised. We have given names of firms from whom some of the pieces may be purchased, with 1941 prices. The methods are grouped under the three general headings: gravity filtration, suction filtration, and pressure filtration.

1. Gravity Filtration. Apparatus required:

1 Micro glass funnel (Fisher Scientific Company, Pittsburgh, Pennsylvania. Catalog No. 20–700, 35 cents each).
1 Pkg. filter paper 4.25-cm. diameter (Whatman #1 Qualitative filter paper. Central Scientific Company, Chicago, Illinois. 15 cents pkg.).

This is conventional filtration on a small scale. Larger funnels and filter paper may be used, but effectiveness decreases as size increases.

2. Suction Filtration. Some form of small side-arm suction flask is needed for all of the alternatives mentioned under this heading. The authors have found the 13-mm. by 130-mm. side-arm test tube quite satisfactory (George T. Walker and Company, Minneapolis, Minnesota. Catalog No. A56-710, 22 cents each).

Alternative (*a*) uses the side-arm test tube with the micro funnel and filter paper mentioned under *1*. The opening in the apex of the funnel is so small that suction will not rupture the unsupported filter paper. The authors personally prefer this assembly to those below.

Alternative (*b*). This scheme is the same as *2*(*a*) except for the use of a small porcelain Büchner or Hirsch funnel (Central Scientific Company, Chicago, Illinois, No. 22894 Büchner, Coors, Porcelain funnel, 70 cents each. Same firm, No. 22896, Hirsch, Coors, Porcelain funnel, 50 cents each). This alternative is quite satisfactory except for the fact that filter paper of the required size cannot be purchased but must be cut individually with cork borers.

Alternative (*c*) is exactly like (*a*) except that a small square of cloth is folded with the paper, on the *outside*, so that when placed in the glass funnel the tip of the paper will be protected from rupture by the suction. This is an old expedient in macro-scale suction filtration.

3. Pressure Filtration. Alternative (*a*).[2] (All of the apparatus may be purchased from the George T. Walker Company, Minneapolis, Minnesota.)

Pressure filter tube (Catalog No. A56-730, 15 cents each).
Vacuum-pressure rubber bulb (Catalog No. A56-740, 25 cents each).

The pressure filter tube is shaped like a centrifuge tube, with a small opening in the bottom and a flared top. A small cotton or glass-wool plug is placed in the small end of the filter tube, which is suspended in a 13-mm. by 130-mm test tube and the liquid forced through the filter by pressure from the bulb. This alternative has the advantage of not requiring suction.

Alternative (*b*) was suggested by H. E. Vermillion, of Beacon, New York. Insert a small cotton plug in the small opening of a medicine dropper, introduce the liquid to be filtered, replace the rubber bulb. Squeezing the bulb forces the liquid through the cotton filter. Although this is rather a "makeshift" scheme, it is inexpensive and serves many a useful purpose under "emergency" conditions. For example, we have found it very helpful for the removal of the occasional precipitates of low density, such as free sulfur, that do not respond readily to centrifuging.

We have personally tried all of the schemes here listed and find that all of them are entirely practical but somewhat slower than centrifuging.

[1] Excerpt from the forthcoming M.S. thesis of Floyd O. Krause, Chemistry Department, State University of Iowa (1942).

[2] BARBER, *Ind. Eng. Chem., Anal. Ed.*, **12**, 58 (1940).

Fishermen note: It is reported that synthetic angleworms are being molded out of rubber and filled with paste flavored with fish eggs.

Carbonyl Compounds as Oxidizing Agents[1]

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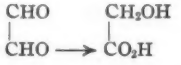
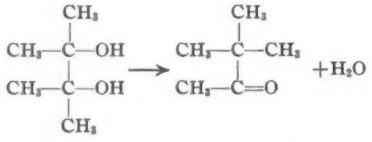
PERHAPS the most general type of reaction in chemistry is that which involves oxidation and reduction. In many reactions of this type both the oxidant and reductant are organic compounds. The Tishschenko and Cannizzaro reactions of aldehydes, *i. e.*,

$$RCHO + RCHO \longrightarrow RCO_2CH_2R \longrightarrow RCO_2NA + RCH_2OH$$

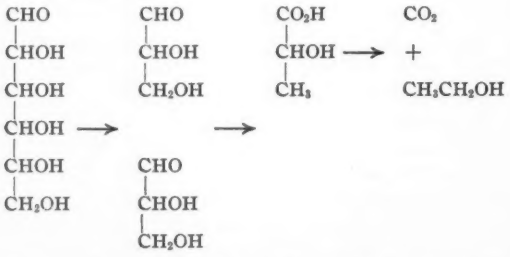
are two of the best known illustrations of such a transformation. The same type of change may occur within a single molecule, for glyoxal is readily transformed to glycollic acid,



If a carbon–carbon bond is broken in such a reaction, an intramolecular rearrangement, a dismutation, or a disproportionation takes place. For example, the pinacolone rearrangement is essentially an intramolecular oxidation-reduction,



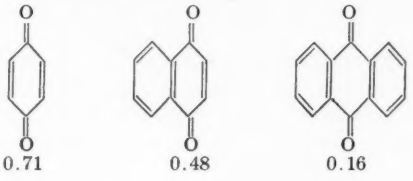
The fermentation of glucose into ethyl alcohol and carbon dioxide is essentially a series of such inter- and intramolecular oxidations and reductions and disproportionations, *e. g.*,



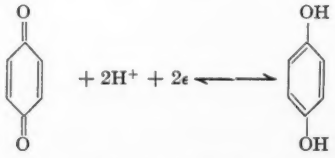
The course and extent of reactions of these types may be said to depend upon the oxidation and reduction potentials of the various compounds and groups involved. It therefore is of interest to note the effect of structure upon the oxidizing power of carbonyl groups.

The most powerful oxidizing agents among the ketones are the quinones related to benzene. For example, *p*-benzoquinone will quantitatively oxidize any of the simple alcohols, being itself converted to hydroquinone.

It has been found convenient to state the strength of *p*-benzoquinone as oxidizing agent with respect to hydrogen. The value is expressed in volts and is calculated from the potential set up at a platinum electrode immersed in hydrogen and an acid solution of the quinone and hydroquinone. The oxidation potential so expressed for three representative quinones is 0.71 for *p*-benzoquinone, 0.48 for 1,4-naphthoquinone, and 0.16 for 9,10-anthraquinone.[2]



The system



is a perfectly reversible one, as otherwise the oxidizing power of *p*-benzoquinone could not be directly compared to hydrogen as a reducing agent. Such a direct measurement is not possible with the simple ketones and aldehydes.

However, it has been ascertained that ketones may be compared against each other as to strength as oxidizing agents even if they cannot be compared directly against hydrogen. This comparison may be made by making use of the reaction

$$R_2CO + R'_2CHOH \longleftrightarrow R_2CHOH + R'_2CO$$

An alcohol and a ketone do not react when simply mixed together, but if the aluminum alkoxide of the alcohol is used the reaction may take place at room temperature and rather rapidly at 100° or less. Since it is often inconvenient to prepare an alkoxide by reaction of aluminum with the alcohol, it may be made by a double decomposition reaction. To this end aluminum *tert*-butoxide is made up in quantity and sufficient of it added to a solution of the alcohol to be oxidized so that the latter is converted at least in part to the alkoxide according to the reaction

$$Al(OC_4H_9\text{-}tert)_3 + 3R'_2CHOH \longleftrightarrow Al(OCHR'_2)_3 + 3tert\text{-}C_4H_9OH$$

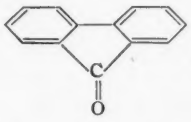
The tertiary alcohol set free is not oxidized and so does

[1] Presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 9, 1941.

[2] CONANT AND FIESER, *J. Am. Chem. Soc.*, **46**, 1859 (1924).

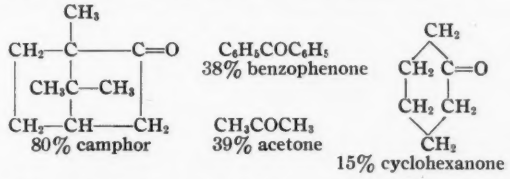
not modify the concentrations at equilibrium in the oxidation-reduction reaction referred to above.

About thirty ketones have been compared as oxidizing agents by this process.[3] Fluorenone has proved to be a good basis of comparison for it reacts rather rapidly without side reactions.



The variation between ketones as oxidizing agents is illustrated by the concentrations of cyclohexanone and of camphor when in equilibrium with fluorenone. If an equimolecular mixture of fluorenone and borneol were mixed there would be at equilibrium 80 per cent camphor, while if a similar mixture of fluorenone and cyclohexanol were made up there would be at equilibrium a 15 per cent yield of cyclohexanone. That is to say, cyclohexanone is a much stronger oxidizing agent than is fluorenone, while camphor is a very poor oxidizing agent.

Acetone and benzophenone are more powerful oxidizing agents than fluorenone but much weaker than cyclohexanone. An equimolecular mixture of fluorenol and acetone (or benzophenone) would, after equilibrium was established, contain 38 to 39 per cent of acetone (or benzophenone) and 61 to 62 per cent fluorenone.



The concentration of the ketones at equilibrium in the studies referred to just above is most conveniently determined by means of the polarograph. This tool requires only a few hundredths of a milligram for an analysis and repeated analyses may be made upon the same sample.

A polarograph is an instrument which continuously increases the potential across a cell, at the same time making a record of the amount of current passing through the cell. The cell is a small glass vessel containing 0.01 to 5.00 ml. of a solution to be analyzed. A stream of fine drops of mercury flows from a capillary (cathode) through the solution to the floor of the cell, which is covered with mercury (anode).

A considerably increased amount of current flows through the cell after the potential across it has reached a value characteristic of the most readily reducible compound in the cell. The amount of current flowing then increases rapidly with a small increase in potential across the cell. During this time is drawn the *A* portion of the curve, as indicated in Figure 1. This portion of the curve is terminated when the amount of current passing through the cell no longer materially increases with increase in potential. When the potential across the cell has reached a value characteristic of the second most readily reducible compound, again the amount of current rapidly increases with increase in potential and the *B* portion of the curve is drawn. The *B* portion of the curve is terminated when the amount of current passing through the cell no longer increases with increase in potential. There is then no considerable increase in current with increase in potential until the potential characteristic of the third most readily reducible compound is reached and the *C* portion of the curve is drawn.

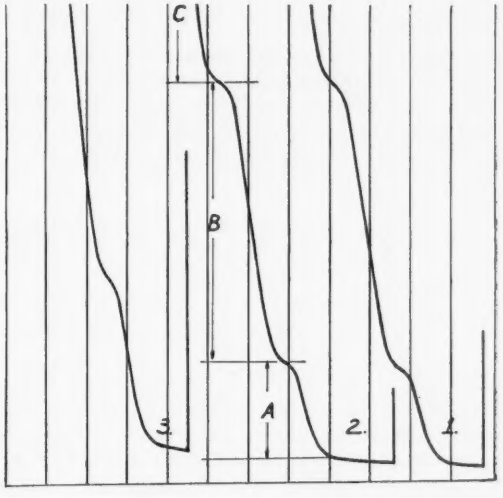


FIGURE. 1.—POLAROGRAMS

The above is a reproduction of a photograph of polarograms. Curves 1 and 2 are duplicate polarograms made on the same sample, while curve 3 is on the same sample at increased sensitivity, using the Leeds and Northrup instrument.

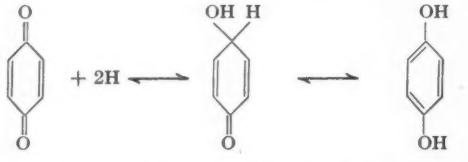
The polarograph is important, in connection with the oxidation potential of ketones, not only because it provides a convenient method of analysis of mixtures but also because in certain instances it gives an independent method of ascertaining the oxidation potential directly. The depolarization potential at the middle of the *B* portion of the curve is characteristic of the particular ketone (in this case acetophenone). This value is called the half-wave potential. All the α-β-unsaturated carbonyl compounds such as quinones, acyl ketones, mesityl oxide, benzal acetone, etc., give "breaks," *i. e.*, depolarization potentials on the polarograph. However, only in the case of the quinones can a true oxidation potential be calculated from the depolarization or half-wave potential.

To summarize, it may be said that quinones give values, at the platinum-hydrogen electrode and at the dropping mercury electrode, which indicate the strength of the compound as an oxidizing agent, while the satu-

[3] For references see BAKER AND ADKINS, *J. Am. Chem. Soc.*, **62**, 3305 (1940).

rated ketones do not give significant values at either electrode. The unsaturated ketones do not give values at the platinum-hydrogen electrode but do show characteristic depolarization potentials at the dropping mercury electrode. However, the values of the depolarization potential do not indicate the strength of the ketone as an oxidizing agent.

A reaction is involved when a quinone accepts hydrogen from another compound, which does not occur when a monoketone accepts hydrogen. The difference lies in the fact that the alcohol from the ketone is stable while that from the quinone undergoes intramolecular rearrangement, *i. e.*,



p-Benzoquinone is a very much more powerful oxidizing agent than is any ketone. This has been ascribed to the fact that the unsaturation of the quinone has enhanced the power of the carbonyl group as an oxidizing agent. However, there is almost no difference in oxidizing power between methyl phenyl ketone and methyl cyclohexyl ketone or between acetone and diphenyl ketone, so that it seems doubtful whether unsaturation has much effect upon the oxidation potential of a carbonyl group.

It seems probable that unsaturation does play a role in determining the extent of the rearrangement of the first formed keto alcohol to the phenol. Thus, one would account for the difference in the oxidation potentials of *p*-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone upon the basis of the effect of the fused rings in stabilizing the keto alcohol produced by reduction. In fact, the oxidation potential of 9,10-anthraquinone is of the same order of magnitude as many of the readily available ketones.

The similarity of 9,10-anthraquinone to ketones as an oxidizing agent has made it possible to compare the oxidizing power of the simple ketones against anthraquinone by the equilibrium method. For example, an equilibrium mixture of anthraquinone, anthrahydroquinone, fluorenone, and fluorenol contained 53 per cent fluorenone and 47 per cent of the quinone. Now, since the oxidation potential of 9,10-anthraquinone has been determined directly against the platinum-hydrogen electrode it is possible to calculate the oxidation potential of fluorenone in terms of volts as compared with hydrogen. Since the ketones have been compared with each other it is possible to assign an oxidation potential to each ketone.

The values of E_0, the oxidation potential expressed in volts, offer the most convenient figures for comparing the oxidation of a series of compounds. However, the fact that the values of E_0 are functions of the equilibrium constant tends to obscure an easy visualization of the real difference in concentration at equilibrium, consequent upon a given difference in the oxidation potentials of two ketones. A few figures will therefore be given to illustrate this relationship.

If a mol of ketone A and of the alcohol corresponding to ketone B are allowed to react and if ketone A has a potential 10 millivolts greater than ketone B, then at equilibrium there will be 0.595 mol of ketone B. If A has a potential greater than B by 20, 50, 75, or 100 millivolts then the mols of B at equilibrium will be 0.685, 0.875, 0.950, or 0.980, respectively. It is obvious that almost quantitative oxidation can be attained if the oxidizing agent has a potential 100 millivolts greater than the ketone to be produced. The enormous difference in oxidizing power among the carbonyl compounds is shown by the fact that at equilibrium there would be 10^{16} as many molecules of camphor as there would be of diphenoquinone, assuming that equimolecular amounts of the quinone and borneol were allowed to react.

The figures listed in Table 1 for the oxidation potentials speak for themselves and require no extended exposition. Perhaps one of the most striking facts is the diversity in structure among ketones which have similar oxidation potentials. The potentials of seventeen of the ketones listed lie within a range of 20 millivolts. The potentials of benzophenone and acetone are almost identical. In fact, anthraquinone, xanthone, cyclopentanone, and dimethyl, diphenyl, and isopropyl phenyl ketones are all within the range 159 ± 5 millivolts, yet the list includes a quinone and diaryl, dialkyl, alkyl aryl, cyclic, unsaturated, and saturated mono-

TABLE 1

SUMMARY OF RESULTS*

Carbonyl Compound	E_0
Camphor	0.115
Di-isopropyl ketone	0.133
Di-*n*-butyl ketone	0.134
Di-*n*-propyl ketone	0.134
Di-isobutyl ketone	0.135
Diethyl ketone	0.143
n-Propyl phenyl ketone	0.146
Methylcyclohexyl ketone	0.149
n-Butyl phenyl ketone	0.149
n-Amyl phenyl ketone	0.150
Fluorenone	0.150
Methyl phenyl ketone	0.151
Ethyl phenyl ketone	0.151
Methyl *tert*-butyl ketone	0.154
Anthraquinone	0.154
Methyl ethyl ketone	0.156
Methyl isopropyl ketone	0.156
Cyclopentanone	0.156
Xanthone	0.157
Isopropyl phenyl ketone	0.158
Dimethyl ketone	0.162
Diphenyl ketone	0.163
1-Chloroanthraquinone	0.168
Phenyl benzyl	0.168
Cyclohexanone	0.195
Benzaldehyde	0.197
tert-Butyl phenyl ketone	0.202
Methyl ether of benzoin	0.232
ω-Methoxy acetophenone	0.246
9,10-Phenanthrenequinone	0.460
1,4-Naphthoquinone	0.484
1,4-Benzoquinone	0.715
Diphenoquinone	0.954

* The values for the quinones were determined by J. B. Conant and Louis Fieser, while those for the ketones are from the work of Fred W. Cox, Robert H. Baker, and Alfred G. Rossow.

ketones. However, cyclohexanone and *tert*-butyl phenyl ketone are very much more powerful oxidizing agents than are the other ketones investigated. These two ketones do not resemble each other in structure but have similar oxidation potentials. The greater strength of cyclohexanone as an oxidizing agent as compared with an open-chain ketone of similar molecular weight is brought out by the figures that if an equilibrium were set up between cyclohexanone and dipropyl ketone there would be 8 per cent of the total ketones present as cyclohexanone and 92 per cent as dipropyl ketone.

At the lower end of the series of ketones is camphor, which, despite the fact that it may be regarded as a substituted cyclohexanone, is 80 millivolts weaker than cyclohexanone itself. Perhaps the most striking effect of structure is that a methoxy group in the α-position with respect to a carbonyl group raises the oxidation potential of the carbonyl by almost a hundred millivolts.

The foregoing discussion has dealt with the energy relationships in oxidation with carbonyl compounds. There are also great differences in the rate and mechanism of reaction of compounds. There is no correlation between rate of reaction and extent of reaction, as a ketone with one of the highest oxidation potentials reacted the most slowly.

The Indicator Method of Classifying Acids and Bases in Qualitative Organic Analysis[1]

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INTRODUCTION

BEFORE attempting to detect the functional groups present in an unknown organic compound, it is convenient to classify the substance in one of several large divisions chiefly on the basis of its acid-base properties. For this purpose, Huntress and Mulliken (*1*) recommend titration of 0.100-g. samples with standard sodium hydroxide and hydrochloric acid. Carboxylic acids are distinguished from phenols by the sharpness of the phenolphthalein endpoint. Kamm (*2*) and Shriner and Fuson (*3*) classify water-insoluble substances by their solubilities in aqueous sodium hydroxide and hydrochloric acid. In this method, carboxylic acids are distinguished from phenols by the solubility of the former in sodium bicarbonate solution.

CRITIQUE OF THE SOLUBILITY METHOD

A difficulty in using the solubility method of classification is illustrated by the case of stearic acid, which, though it possesses about the same acid strength as benzoic acid, fails to dissolve in sodium bicarbonate solution. Likewise some phenols (*4*) and sulfonamides (*5*, *6*) are known which do not dissolve in aqueous sodium hydroxide. Among the bases, triphenylguanidine does not disclose its basicity in aqueous hydrochloric acid, although a much weaker base, N-ethylacetanilide, does. One reason for these discrepancies is that the ability of an acid or a base to dissolve in aqueous alkali or acid, respectively, depends not alone on its acid or base strength, but also on its intrinsic solubility in water, that is, on its ability to dissolve as an unionized molecule. This situation may be elucidated as follows.

Factors Governing the Solubility of Acids in Aqueous Sodium Hydroxide.—If a solid, slightly soluble, weak, or intermediate acid, HA, is suspended in water, two equilibria become established: (1) the *solubility equilibrium* between the undissolved acid, HA_u, and the dissolved acid, HA_d; and (2) the *acid-base equilibrium* between the dissolved acid and the solvent. These interlocking equilibria lead to an expression for the observed solubility, S, which includes the intrinsic solubility (*i. e.*, the solubility due to the unionized acid), K_s, and the acidity constant, K_a.

$$\begin{matrix} HA_u \\ \downarrow\uparrow \\ HA_d \end{matrix} + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (1)$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA_d]} \qquad (2)$$

Hence

$$[A^-] = \frac{K_a\,[HA_d]}{[H_3O^+]} \qquad (3)$$

The observed solubility, S, comprises the concentration of the unionized acid, $[HA_d]$, as well as that of its conjugate base, $[A^-]$, hence

$$S = [HA_d] + [A^-] \qquad (4)$$

$$S = [HA_d] + \frac{K_a\,[HA_d]}{[H_3O^+]} \qquad (5)$$

$$S = [HA_d]\left(1 + \frac{K_a}{[H_3O^+]}\right) \qquad (6)$$

[1] Presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 11, 1941.

Since HA_d is in equilibrium with the undissolved acid, the concentration of HA_d is constant at a given temperature and may be set equal to K_s. K_s represents the *intrinsic solubility* or the solubility which the acid would have if no acid-base reaction occurred. In most cases it does not differ materially from the solubility of the acid in water. Hence, the final expression,

$$S = K_s\left(1 + \frac{K_a}{[H_3O^+]}\right) \qquad (7)$$

indicates that the observed solubility of a slightly soluble acid in alkali of a given pH is not only dependent on its acidity constant but is also directly proportional to its solubility in water.

The significance of equation 7 may be illustrated by means of a numerical example. Consider a slightly soluble, monobasic acid of molecular weight 250. If 0.10 g. of this substance is to dissolve in 4 ml. of molar sodium hydroxide, the resulting solution will be approximately 0.1 *M* with respect to the acid-base system (in its acid and conjugate base forms) and approximately 1 *M* with respect to hydroxyl ion [hence, 10^{-14} *M* with respect to hydronium (or oxonium) ion]. Substitution of these values into equation 7 leads to a relationship between K_s and K_a (equation 8) which

$$K_s = \frac{0.1}{1 + \frac{K_a}{10^{-14}}} \qquad (8)$$

permits the calculation of the minimum intrinsic solubility required for acids of various given strengths in order that the solubility test, as defined above, may succeed. Values obtained in this way are given in Table 1 (upper column headings).

TABLE 1

REQUIRED RELATIONSHIP BETWEEN ACID STRENGTH AND INTRINSIC SOLUBILITY IN THE SOLUBILITY TESTS FOR ACIDS AND BASES IF A SLIGHTLY SOLUBLE, MONOBASIC ACID OR MONOACIDIC BASE IS TO FORM A 0.1 *M* SOLUTION IN *M* NaOH OR HCl, RESPECTIVELY

Acids	pK_a	$\log \frac{K_a}{10^{-1}}$	*Minimum* K_s	*Minimum Intrinsic Solubility for an Acid of Molecular Weight 250*
	5	9	10^{-10} *M*	0.000000025 g./l.
	10	4	10^{-5}	0.0025
	12	2	0.0010	0.25
	13	1	0.0091	2.3
	14	0	0.05	12.5
Bases	pK_i*	pK_a	*Minimum* K_s	*Minimum Intrinsic Solubility for a Base of Molecular Weight 250*

* The classical ionization constant for bases.

Factors Governing the Solubility of Bases in Aqueous Hydrochloric Acid.—Considerations similar to those discussed above for acids apply to the solubility test for bases. The corresponding interlocking solubility and acid-base equilibria lead to the following derivation for slightly soluble, intermediate and weak bases.

$$BH^+ + H_2O \rightleftharpoons H_3O^+ + \begin{matrix} B_s \\ \Updownarrow \\ B_d \end{matrix} \qquad (9)$$

$$S = K_s\left(1 + \frac{[H_3O^+]}{K_a}\right) \qquad (10)$$

By way of illustration, consider a slightly soluble, monoacidic base of molecular weight 250. If 0.10 g. of this substance is to dissolve in 4 ml. of *M* hydrochloric acid, the resulting solution will be approximately 0.1 *M* with respect to the acid-base system (in its conjugate acid and base forms) and approximately 1 *M* with respect to hydronium ion. Substitution of these values into equation 10 leads to a relationship between K_s and K_a which permits the calculation of the minimum intrinsic solubility required for bases of various given strengths in order that the solubility test succeed. Values obtained in this way are given in Table 1 (lower column headings).

Factors Governing the Solubility of Acids in Aqueous Sodium Bicarbonate.—In the case of the solubility test for acids with sodium bicarbonate, the problem differs from that of the test with sodium hydroxide discussed previously only in that the buffer system, HCO_3^-:CO_2, is employed in place of the sodium hydroxide buffer. The hydronium ion concentration is thus fixed at about $10^{-6.5}$ instead of at about 10^{-14}. Application of equation 7 to a numerical example similar to those previously discussed yields the results given in Table 2.

TABLE 2

REQUIRED RELATIONSHIP BETWEEN ACID STRENGTH AND INTRINSIC SOLUBILITY IN THE SOLUBILITY TEST FOR ACIDS WITH SODIUM BICARBONATE IF A SLIGHTLY SOLUBLE, MONOBASIC ACID IS TO DISSOLVE IN 0.2 *M* SODIUM BICARBONATE TO FORM A 0.1 *M* SOLUTION

pK_a	$\log \frac{K_a}{10^{-6.5}}$	*Minimum* K_s	*Minimum Intrinsic Solubility for an Acid of Molecular Weight 250*
5	+1.5	0.0030 *M*	0.75 g./l.
10	−3.5	0.10*	25. *

* These figures show that bicarbonate does not enhance the solubility of so weak an acid.

This calculation indicates that for monobasic acids of the strength of acetic acid, those which are less soluble in water than about 0.003 mol per liter will not give solutions as strong as 0.1 *M* in bicarbonate. An example of such an acid is stearic acid. Furthermore, the calculation shows that with acids as weak as pK_a = 10, bicarbonate causes no appreciable enhancement in solubility. Such is the case with β-naphthol.

The Formation of Insoluble Salts.—An experimental difficulty sometimes arises in the testing of solids due to the insolubility of the sodium salts of certain acids in sodium hydroxide or of the hydrochlorides of certain bases in hydrochloric acid. This may cause the original solid to appear not to have reacted. Such difficulty may sometimes be avoided by vigorously stirring the finely powdered sample in an aqueous suspension and gradually adding sodium hydroxide or hydrochloric acid to it. Under these conditions the substance may first dissolve after which the salt in question will precipitate. Examples of substances which exhibit this behavior are *p-tert*-amylphenol and benzidine.

It should be noted at this point that the mere ability of a substance to form an insoluble "salt" in aqueous medium is no measure of its acidity or basicity. Witness the formation of cuprous acetylide and urea nitrate from essentially neutral organic compounds.

In spite of its drawbacks, the solubility method remains of considerable practical value in organic analysis. It is desirable, however, to supplement it by a method which is largely free from its shortcomings and which allows an acid-base classification of water-soluble as well as of water-insoluble compounds. This is provided by the indicator method which will now be discussed.

THE INDICATOR METHOD

Principles of the Indicator Method.—The equilibria which occur when intermediate or weak acids are dissolved in water may be represented as follows.

For Uncharged Acids		*For Cationic Acids*	
$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	(11)	$BH^+ + H_2O \rightleftharpoons H_3O^+ + B$	(11′)
$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$	(12)	$K_a = \frac{[H_3O^+]\,[B]}{[BH^+]}$	(12′)
Hence,		Hence,	
$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$	(13)	$[H_3O^+] = K_a \frac{[BH^+]}{[B]}$	(13′)
In logarithmic notation,		In logarithmic notation,	
$pH = pK_a - \log \frac{[HA]}{[A^-]}$	(14)	$pH = pK_a - \log \frac{[BH^+]}{[B]}$	(14′)

If half of the dissolved acid is converted to its conjugate base or if half of the base taken is converted to its conjugate acid, the final terms in equations 14 and 14′ disappear and the equations become

$$pH = pK_a \qquad (15)$$

The pH of such a half-neutralized solution is not sensitive to changes in the concentrations of the conjugate acid and base. Thus when the portion of the acid-base system which is present as the conjugate base varies between 9 and 91 per cent,

$$pH = pK_a \pm 1 \qquad (16)$$

Consequently it is possible to obtain an approximate estimate of the strength of an acid or a base by noting the pH of its partially neutralized solution. For this purpose acid-base indicators are most convenient.

An Indicator Reagent for Classifying Acids.—As is shown in Table 3, organic acids may be classified in three divisions: *strong acids* ($pK_a = <2$) typified by sulfonic acids, *intermediate acids* ($pK_a = 2$–7) typified by the carboxylic acids, and *weak acids* ($pK_a = 8$–12) typified by the phenols (7). Hence, an indicator such as thymol blue ($pK_a = 1.7$) with a color change from red to yellow may serve to distinguish between the buffers resulting from strong and intermediate acids; while bromothymol blue ($pK_a = 7.3$) with a color change from yellow to blue may be employed to discriminate between the buffers prepared from intermediate and weak acids. Since the colors of these two sulfonphthaleins are not antagonistic they may be mixed in a single reagent. If, furthermore, the reagent contains the potassium hydroxide necessary to convert acids to buffer mixtures, it may be used directly to classify acids.

TABLE 3
CLASSIFICATION OF ACID-BASE STRENGTHS

pK_a	*Conjugate Acid*	*Conjugate Base*	*Examples of Acid-Base Systems*
<2	Strong (A_s)	Neutral (N)	$RSO_3H:RSO_3^-$
			$Ar_2NH_2^+:Ar_2NH$
2–7	Intermediate (A_i)	Weak (B_w)	$CH_3COOH:CH_3COO^-$
			$ArNH_2^+:ArNH_2$
8–12	Weak (A_w)	Intermediate (B_i)	$ArOH:ArO^-$
			$CH_3NH_2^+:CH_3NH_2$
>12	Neutral (N)	Strong (B_s)	$CH_3OH:CH_3O^-$
			$(NH_2)_2C=NH_2^+:(NH_2)_2C=NH$

In order to apply such an indicator reagent generally it must be made up, not in water, but in some organic solvent such as methanol. As long as acids of the uncharged type alone are considered, this occasions no difficulty, since the indicators employed manifest about the same shift in acidity in methanol as do the uncharged acids (*8*). With cationic acids, however, this is not the case since much smaller shifts in acidity are the rule with these acids.

This leads to the danger of overlapping. Thus, for example, in water, anilinium ion ($pK_a = 4.6$) and acetic acid ($pK_a = 4.8$) lie close together in the intermediate acid range, while ammonium ion ($pK_a = 9.3$) and phenol ($pK_a = 9.9$) are close together in the weak acid range (Figure 1). In methanol (at an ionic strength of 0.05), however, acetic acid ($pK_a = 9.1$) drops away from the anilinium ion ($pK_a = 6.1$) and, likewise, phenol ($pK_a = 13.5$) drops away from the ammonium ion ($pK_a = 10.7$). The result is that acetic acid, an *intermediate* acid in water, and ammonium ion, a *weak* acid in water, approach each other in methanol. In water, bromothymol blue ($pK_a = 7.3$) falls about midway between the anilinium ion–acetic acid pair and the ammonium ion–phenol pair. In methanol, the indicator ($pK_a = 11.3$) still falls about midway between acetic acid and phenol. Anilinium and ammonium ions, however, are both on the acid side of the indicator, although ammonium ion is close enough to the indicator to overlap its range to some extent. For these cationic acids, bromocresol purple, which is about one unit more acidic than bromothymol blue (pK_a, in water = 6.4; in methanol = 10.2) is more satisfactory, but, on the other hand, this indicator overlaps the ranges of the weakest *intermediate* acids (uncharged types such as vanillin and anionic types such as bisuccinate ion).

Despite the difficulty due to the dispersion of the weak and intermediate acids on passing from water to methanol (Figure 1), it seems desirable to retain, as far as possible, a classification based on the behavior of the acids in water. This may be accomplished by the expedient of using a mixture of bromocresol purple and bromothymol blue for distinguishing between weak and intermediate acids. Because of its dichromatism (the property of exhibiting different colors in layers of different thickness) bromocresol purple makes it possible to mark the region of pK_a's between 10–11 in methanol. In solutions more acid than 10, both bromocresol purple and bromothymol blue exhibit yellow colors. Between 10 and 11, bromothymol blue remains yellow while bromocresol purple manifests its

dichromatic purple form. Beyond 11, the blue form of bromothymol blue overpowers the dichromatism of the other indicator and the reagent appears blue violet.

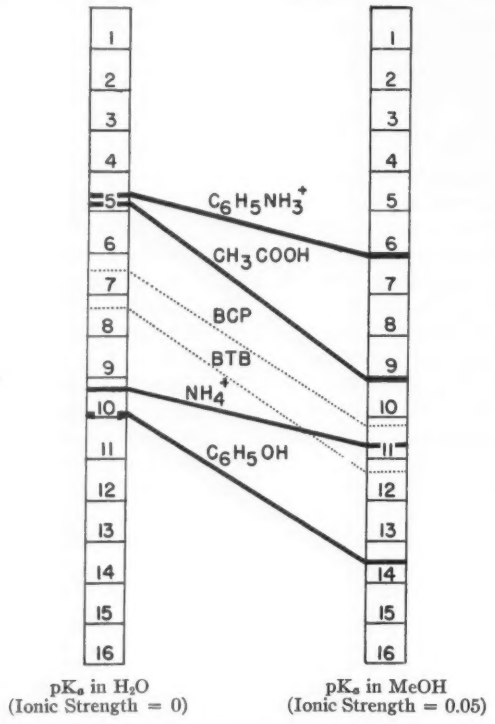


FIGURE 1.—ACIDITY "LADDERS" IN WATER AND METHANOL

This use of overlapping indicators broadens the boundary line between weak and intermediate acids but it serves to prevent the weakest of the intermediate acids (some A_i° and most A_i^-) from being confused with most weak acids, and the strongest of the weak acids (some A_w^+) from being confused with most intermediate acids.

The resulting complete indicator reagent for classifying acids (Reagent A-II) consists of $M/20$ potassium hydroxide in methanol containing thymol blue, bromocresol purple, and bromothymol blue. This solution is blue violet in color. If about 30 mg. of an acid is dissolved in a ml. of this reagent, the color will either not change or be converted to yellow, dichromatic purple, or red, depending on whether the acid is weak, or intermediate, or strong (Table 4).

An Indicator Reagent for Detecting Acids.—The reagent described above may be employed to *classify* acids but does not distinguish weak acids from nonacidic substances. To achieve this discrimination or, in general, to *detect* acids, another reagent is required, the composition of which is based on the following considerations. A 0.01 M aqueous solution of potassium hydroxide has a pH of 12. If two equivalents of an acid of, say, pK$_a$ = 5 are added to this solution, the pH will become 5. If, however, acids with pK$_a$'s in the vicinity of, or greater than 12 are added, no appreciable change in pH occurs. That is to say, all acids weaker than about pK$_a$ = 12 appear to be equally weak in this solution. Now, in order that an indicator transform to its acid color at pH = 12, its pK$_a$ must be somewhat greater than 13 (equation 14). Since an indicator of this strength is largely in its *acid* form at pH 12, it cannot be used to detect acids in the solution under consideration. In essence this situation is due to the competition between the acidity of the solvent and that of the added acid. A less acidic (or more basic) solvent would obviate this competition and permit the discrimination desired. Pyridine serves well for this purpose, but, on the other hand, limits the acid strengths which may be discriminated to those which are weaker than pyridinium ion (pK$_a$ = 8.6). This leveling effect is portrayed graphically in Figure 2 by plotting the pK$_a$'s of acids in water against their pK$_a$'s in a more basic solvent such as pyridine.

In practice a reagent consisting of a 1:1 mixture of pyridine and methanol which is 0.05 M with respect to potassium hydroxide and contains alizarin yellow R and bromothymol blue (Reagent A-I) serves to *detect* acids. The bromothymol blue functions by emphasizing the color change of the alizarin yellow R. Thus, the latter indicator alone shows a color change from red to orange yellow, but in the presence of the blue sulfonphthalein these colors become purple and green,

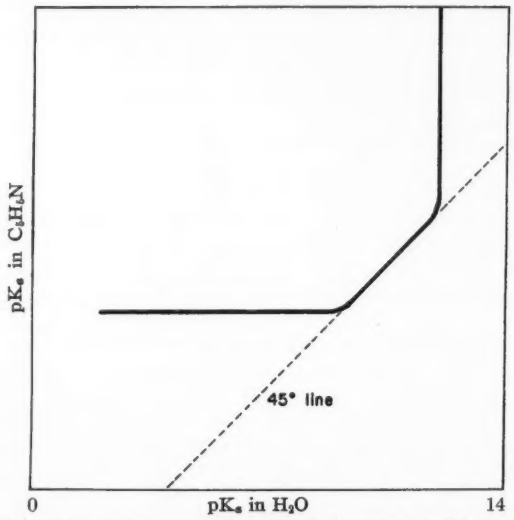


FIGURE 2.—RELATIONSHIP BETWEEN ACIDITIES IN WATER AND IN PYRIDINE (SCHEMATIC)

Note that to the right of a certain point, acids which are widely separated in pyridine are all of the same acidity in water; and that to the left of another point, acids which are widely separated in water all have the same acidity in pyridine.

respectively. In addition, the second indicator allows a partial classification, since strong and intermediate acids exhibit a yellow color while weak acids show a green. The results to be obtained with the two indicator reagents for acids are summarized in Table 4.

TABLE 4

INDICATOR REAGENTS FOR ACIDS

A-I. *M*/20 KOH in Pyridine-Methanol + Alizarin Yellow R and Bromothymol Blue	yellow		green	purple
A-II. *M*/20 KOH in Methanol + Thymol Blue + Bromocresol Purple and Bromothymol Blue	red	yellow *	blue-violet	
Divisions	*Strong Acids* (A_s)	*Intermediate Acids* (A_i)	*Weak Acids* (A_w)	*Non-Acids*

* Purple dichromatic zone characteristic of bromocresol purple. Here are found the weakest of the uncharged or anionic A_i as well as the strongest of the cationic A_w.

Indicator Reagents For Bases.—The same principles which have been discussed above for acids apply to the study of bases. Here also two reagents are required: one to *detect* the bases and the other to *classify* them. Just as a more basic solvent than methanol is used for the detection of acids, so a more acidic solvent than methanol is desirable for the detection of bases (Figure 3). For this purpose glacial acetic acid is satisfactory (*9*). The first reagent for bases (Reagent B-I) consists of *M*/20 *p*-toluenesulfonic acid in glacial acetic acid and contains the indicator, benzeneazodiphenylamine, together with methylene blue. The latter has no indicator properties but serves to emphasize the color change of the active indicator. Alone, benzeneazodiphenylamine changes from red to orange yellow. In the presence of methylene blue the color change becomes the readily perceivable purple to green.

The second reagent for bases (Reagent B-II) consists of *M*/20 hydrochloric acid in methanol plus the indicators, thymol blue, bromocresol purple, and bromothymol blue. That the same indicators may be used for classifying both acids and bases follows from the reciprocal relationship between acids and bases shown in Table 3; *i. e.*, A_s–N, A_i–B_w, A_w–B_i, and N–B_s. The indicator reagents for bases are summarized in Table 5.

TABLE 5

INDICATOR REAGENTS FOR BASES

B-I. *M*/20 *p*-Toluenesulfonic Acid in Glacial Acetic Acid + Benzeneazodiphenylamine and Methylene Blue	green			purple
B-II. *M*/20 HCl in Methanol + Thymol Blue + Bromocresol Purple and Bromothymol Blue	blue-violet	*	yellow	red
Divisions	*Intermediate Bases* (B_i)		*Weak Bases* (B_w)	*Non-Bases*

* Purple dichromatic zone characteristic of bromocresol purple. Here are found the weakest of the uncharged B_i and the strongest of the anionic B_w.

The Behavior of Ampholytes.—The behavior of ampholytes toward the indicator reagents is of interest. These substances give positive tests with both the A-I and the B-I reagents, and may even be classified further by the A-II and B-II reagents. Thus, aromatic and heterocyclic amino acids such as *p*-aminobenzoic and nicotinic acids test as intermediate acids *and* weak bases. Aliphatic amino acids like glycine fall into the weak acid-weak base class. Sulfanilamide behaves similarly. Salts of intermediate or weak bases with intermediate or weak acids, such as ammonium benzoate, for example, also exhibit both acidic and basic properties, as do also the primary salts of dibasic acids, such as potassium hydrogen phthalate, or of diacidic bases such as the monohydrochlorides of diamines.

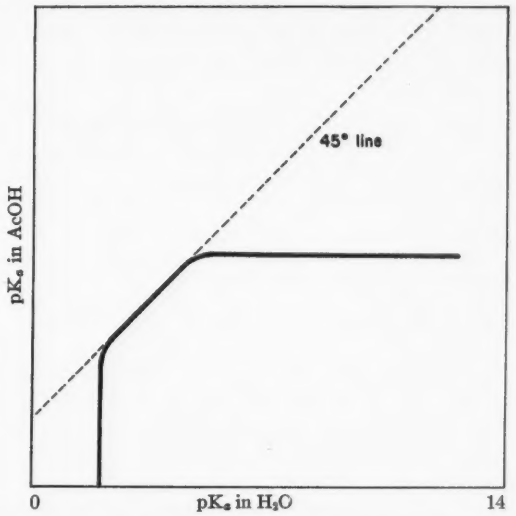
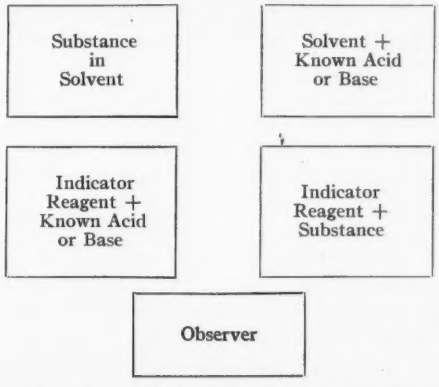


FIGURE 3.—RELATIONSHIP BETWEEN ACIDITIES IN WATER AND IN ACETIC ACID (SCHEMATIC)

Note that to the left of a certain point, acids which are widely separated in acetic acid all have the same acidity in water; and that to the right of another point, acids which are widely separated in water all have the same acidity in glacial acetic acid.

Anomalous Cases in the Indicator Method.—Deeply colored compounds may interfere with the use of the indicator reagents by obscuring the indicator colors. When the color of the indicator is not completely obscured the four-tube method may be employed.


Substance in Solvent
Solvent + Known Acid or Base
Indicator Reagent + Known Acid or Base
Indicator Reagent + Substance
Observer

If the substance under examination shows indicator properties it may be classified by making up a special reagent containing *M*/20 potassium hydroxide or hydrochloric acid in methanol together with the substance as indicator and then adding substances of known acidity which lie near the borderlines of the divisions, such as 2,4-dichlorophenol.

Comparison of the Solubility and Indicator Methods.—While in many cases the classification obtained by the solubility method will coincide with that obtained by the indicator method, there are numerous instances in which divergent results are obtained. Some examples of these are given in Table 6.

TABLE 6

COMPARISON OF THE INDICATOR AND SOLUBILITY METHODS

Substance	*Solubility Method*	*Indicator Method*
Crotonic acid	H_2O-sol., Et_2O-sol.	A_i
Malic acid	H_2O-sol., Et_2O-ins.	A_i
Cinnamic acid	A_i	A_i
Bromopalmitic acid	N	A_i
Phenol esters	N	A_w
β-Diketones	N	A_w
Benzoin	N	A_w
N-Ethylacetanilide	B	N
p-Aminodiphenyl	N	B_w
Triphenylguanidine	N	B_i

This discussion may be concluded by presenting the classes of organic compounds found in each of the six divisions of acids and bases which result from the use of the indicator method of preliminary classification. These are:

Weak Bases: Aromatic hydrazines; azomethines, etc.; primary, secondary, and tertiary aromatic amines; heterocyclic amines of the pyridine type; some oximes; and alkali and alkaline-earth salts of intermediate acids.

Intermediate Bases: Aliphatic hydrazines; primary, secondary, and tertiary aliphatic amines; heterocyclic amines of the piperidine type; amidines and guanidines[2]; alkali and alkaline-earth salts of weak acids and neutrals.[3]

Weak Acids: Phenols; phenol esters; β-keto-esters, etc.; α-hydroxyaldehydes and ketones; α-ketoaldehydes; primary and secondary nitroparaffins; polynitroaromatic compounds (such as trinitrotoluene, 2,4-dinitroaniline, etc.); hydroxamic acids; some oximes; imides and ureides; mercaptans, thioamides, and sulfonamides; salts of strong acids with intermediate bases.

Intermediate Acids: Carboxylic acids and anhydrides; some esters; cyclic β-diketones, etc.; phenolic aldehydes and ketones; cyano-, nitro-, and polyhalophenols; aminosulfonic acids; salts of strong acids with weak bases or ampholytes.

Strong Acids: Some carboxylic acids; carboxylic acid chlorides; sulfonic acids; sulfonchlorides; sulfonamides; polynitrophenols; salts of strong acids with neutral compounds; bisulfates of weak and intermediate bases.

Ampholytes: Aminophenols; aminomercaptans; aminosulfonamides, aliphatic and aromatic amino acids; some oximes; salts of weak and intermediate bases with weak and intermediate acids; primary salts of dibasic acids; primary salts of diacidic bases.

[2] Guanidine itself and N-alkyl, N,N-dialkyl, and N,N′,N″-trialkylguanidines are strong bases (*10*).

[3] The latter are strong bases.

PREPARATION OF REAGENTS

Stock solutions of the indicators of 0.1 per cent strength are made up in the appropriate solvent. Concentrated hydrochloric acid, 2 *M* potassium hydroxide in methanol and *M* *p*-toluenesulfonic acid in glacial acetic acid are also required. With these solutions, indicator reagents may be quickly prepared by mixing the relative volumes indicated in Table 7. The reagents should be stored in brown bottles.

TABLE 7

RELATIVE VOLUMES OF STOCK SOLUTIONS EMPLOYED IN PREPARING INDICATOR REAGENTS

Stock Solutions		*A-I*	*A-II*	*B-I*	*B-II*
Alizarin yellow R	(MeOH)	25			
Bromothymol blue	(MeOH)	25	25		25
Bromocresol purple	(MeOH)		37.5		37.5
Thymol blue	(MeOH)		25		25
Benzeneazodiphenylamine	(AcOH)			25	
Methylene blue	(AcOH)			10	
2 *M* Potassium hydroxide	(MeOH)	25	25		
M *p*-Toluenesulfonic acid	(AcOH)			50	
Conc. hydrochloric acid					4.5
Methanol		425	887.5		908
Pyridine		500			
Glacial acetic acid				915	

PROCEDURE

In the case of liquids and of solids readily soluble in the indicator solvents, one drop or 30 mg. of the sample is added to *one* ml. of the indicator reagent. A second portion of the sample may be added as a check that sufficient substance is present. With solids the finely powdered material may be vigorously stirred with the test solution, or the sample may previously be dissolved in half a ml. of the indicator solvent or of a closely related solvent.

ACKNOWLEDGMENT

The author gratefully acknowledges the material assistance obtained from frequent discussions of the use of indicators with his colleague, Dr. Joseph Steigman.

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Construction of Complex Molecular Models with Application to Carbohydrates

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IN INSTRUCTION or study regarding problems of molecular structure one frequently deals with complicated spatial relations between atoms. If a large number of these are involved, the construction of models from ready-made individual atom balls may be unsatisfactory and expensive. When comparison is to be made of molecules having a common fixed group of atoms, such as an atom ring, or containing a large number of repeating units, as in high polymers, it becomes worth while to attempt to conserve atom models by casting copies of the repeated units from an original model.

The present paper describes a simple method of preparing these copies. Starting with the Fisher-Hirschfelder atom models one can obtain atom groups made to the convenient scale of one cm. per A., with appropriate bond lengths and angles and with the "space-filling" feature. In addition the use of snap fasteners as chemical bonds is readily incorporated, so that one then has rapidly assembled, tightly held units, which also have freedom of rotation about the snap bonds.[3]

PLANNING THE ATOM-GROUP MODELS

Before attempting to construct a satisfactory set of atom groups to illustrate any given class of chemical compounds it is necessary first to discover what is known about the specific configurations (*i. e.*, shapes of atom rings, etc.) and to plan conventions regarding location of male or female snap portions on the various groups. Illustrative of these preliminary processes the case of a system of models for use in considering various carbohydrate problems is outlined. For these chemical substances the application of the casting method is particularly promising: one may wish to visualize differences between optically isomeric pentoses or hexoses; the problem at hand may involve substitution of various groups, as in methylation or ester formation; or models may be made of the polymers, starch and cellulose. In all such cases a fair number of the basic furanose or pyranose rings and attached groups will be required.

While no definite evidence is available, there seems to be no reason for adopting other than the single possible strainless model for the furanose ring, namely that in which the four carbon atoms and the oxygen are coplanar. In considering the pyranose ring, however, one is unfortunately faced with a considerable amount of uncertainty. The following models for the pyranose ring have been described:

1. There are eight strainless forms which can be constructed for any given pyranose sugar (*6*). Scattergood and Pacsu (*8*) give particularly good illustrations of how the eight types of ring appear when formed from the Fisher-Hirschfelder models. The eight forms are based on one "trans" or "chair-shaped" ring and three "cis" or "boat-shaped" rings, each of the four being translatable into two different configurations for a given sugar by numbering the carbon atoms in the two possible directions from the oxygen. It may be worth pointing out that while the trans ring configuration is fixed and cannot be altered without straining bond distances and angles, the three cis models can be transformed continuously from one into any other by simultaneous rotation about bonds. It is, therefore, somewhat of an oversimplification to speak only of the three particular cis forms usually described.

2. Scattergood and Pacsu (*8*) cite reasons for eliminating all but one of the eight models for the aldohexoses. The favored model is based on a trans ring form, arguments being grounded largely in the absence of steric hindrance when —OH, —CH_2OH, and —H groups are placed at proper locations. The only other sterically possible ring found for these sugars is one of the cis forms, but this is rejected as improbable because of the repulsions expected between opposite atoms of the ring and attached groups.

The model for the glucose residue used by Meyer and Misch (*7*) in calculating the intensities of X-ray diffractions from cellulose is essentially the same one favored by Scattergood and Pacsu and used by Caesar and Cushing (*2*) in constructing models for starch.

3. The first direct experimental attempt to answer the question of pyranose ring configuration was that of Cox, Goodwin, and Wagstaff (*3a*). On the basis of experience with X-ray diffraction properties of sugars and derivatives, they suggested a "planar" model, which is, however, only planar with respect to the five carbon atoms, the oxygen being displaced somewhat from the plane of the carbons. This model is similar to that employed by Andress (*1*) in calculating diffraction intensities for cellulose. More recent work of Cox and Jeffrey (*3b*) seems to favor a certain amount of ring puckering.

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[2] Journal Paper No. J-923 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 639.

[3] Subsequent to the formulation of the methods for model construction described in this paper, BLACK AND DOLE described "Molecular models with free rotation," J. CHEM. EDUC., 18, 424 (1941), which also utilize snap bonds.

4. Freudenberg, Schaaf, Dumpert, and Ploetz (*4*) have used one of the cis-shaped ring models to describe the Schardinger dextrins and starch. Their model also is interesting in connection with the characteristic iodine-staining powers of the dextrins and starch. The particular cis ring used by these investigators is one with carbon atoms 1 and 4 in a plane which is different from that containing the other atoms of the ring. While this configuration was discarded by Scattergood and Pacsu (*8*), because of slight steric difficulties involving the —OH and —H on carbon atoms 1 and 4, this is perhaps not serious, particularly in view of the possibility of avoiding the difficulty by slight simultaneous atom rotations about ring bonds, as mentioned above. Also, until the repulsive forces used to discard the cis configurations in general are more definitely known, the possibility of the Freudenberg model cannot be disregarded.

The weight of evidence is perhaps in favor of a configuration somewhere between the planar Cox model and the trans strainless one, as Gorin, Kauzmann, and Walter (*5*) suggest. In making models the Cox configuration is probably to be preferred for purely instructional purposes, since in it the attached groups extend, except for those attached to carbon atoms 1 and 5, symmetrically "above" and "below" the plane of the ring, and hence are placed very closely like they are shown in the conventional "three-dimensional" projection formulas introduced by Haworth (*6*). For more exact considerations it may be well to have at hand ring models corresponding to both the trans and

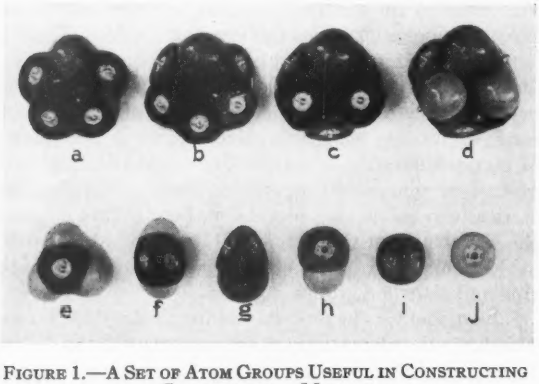


FIGURE 1.—A SET OF ATOM GROUPS USEFUL IN CONSTRUCTING CARBOHYDRATE MODELS

Parts *a* through *d* show single-piece painted plaster copies of atom rings: *a*, furanose ring; *b*, the Cox "planar" model for the pyranose ring; *c*, the "trans" or "chair" model for the same group; and *d*, a trans model with hydrogens attached in such a way as to limit its application to derivatives or polymers of α- or β-glucose (two other hydrogen atoms not visible are on the back face). The smaller groups, described in the text, are: *e*, methyl; *f*, methylene; *g*, carbonyl; *h*, hydroxyl; *i*, double-bonded oxygen bridge; *j*, hydrogen. Black atoms in this and other figures are carbon, light ones hydrogen, those of intermediate shade oxygen.

Cox forms in particular, and in special cases to some of the cis forms.

Having decided on a particular configuration, one proceeds to form a consistent plan for the ring nuclei and groups to be attached to them. The following is an example of a system of conventions found useful in preparing a set of models for carbohydrate study:

(*a*) Whatever the furanose or pyranose ring configuration adopted, all atoms of the ring are to be held fixed and supplied with sufficient appropriately placed *male* snap portions to receive all attached —CH_2OH, —OH, —H or other groups. By leaving all positions open the number of different ring systems needed in a wide variety of applications is considerably reduced. If the models are to be used for more particular purposes some labor can be saved by incorporating with the ring the hydrogen atoms which may remain fixed for all situations of interest and whose rotations are unimportant. Parts *a* to *d* of Figure 1 illustrate various rings of interest.

(*b*) Other groups of importance are: —CH_3 with single male snap, =CH_2 supplied with one male and one female junction each, =CO with male and female unions, —OH with single female snap, =O with two female bond halves, and —H with single female junction. Parts *e* to *j* of Figure 1 show these groups.

With a sufficient number of the constructional elements described above it is possible to build any simple furano- or pyrano-pentose or hexose, any polymer of these, and also any alkyl derivatives or carboxylic esters. Extension to include groups necessary for other carbohydrate derivatives can easily be made.

MAKING THE MODELS[4]

The procedure used in obtaining the plaster copies of any original configuration of atom models may be divided into the following steps:

1. The atom models to be included in one group are temporarily connected as they are to be and the faces from which will issue bonds to other atoms not included in the group are marked. After disassembling the atoms, the marked faces are prepared to receive either male or female portions of snap fasteners of any convenient size. A hole is countersunk into each such face to a depth which will leave the outer mounting surface of the snap flush with or a little below the atom face. Each snap is then cemented into place.

2. The prepared atoms are now permanently fastened together in the desired configuration. Cracks and unnecessary space in the center of a ring, etc., are filled with modeling clay, so that the final appearance of the atom group is obtained, with all unused bonding surfaces containing a portion of snap fastener. Figure 2*a* shows an original model at this stage.

3. In the meantime snaps to go opposite those of the model in the rubber casting form are prepared as

[4] Those contemplating making such models may find helpful the following information regarding sources of some of the materials employed: The Fisher-Hirschfelder atom balls used in constructing the original group models are supplied by the Fisher Scientific Company, Pittsburgh, Pennsylvania. The "liquid live rubber" is obtainable from Stewart's Studio, Lake Geneva, Wisconsin. Snaps used as bonds are of the ordinary dressmaker's type, size 1/0, purchasable at any dry-goods store.

follows: Anchors consisting of wire or thin wings of metal are fastened to the rear of the mounting surfaces (*i. e.*, away from working faces) of the snaps. If the

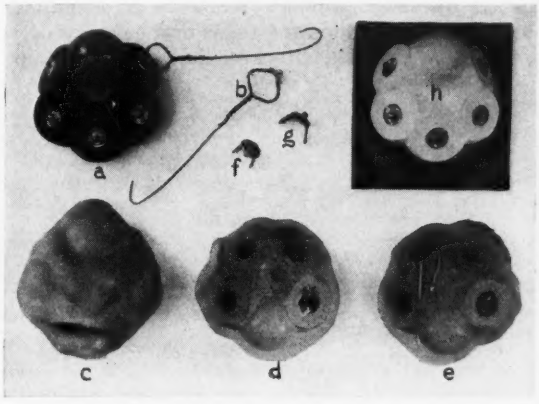


FIGURE 2.—STEPS IN PREPARING PLASTER COPIES OF AN ATOM GROUP

a, the original Fisher-Hirschfelder model for a Cox pyranose ring, prepared by straining the bond angles into the "planar" configuration; *b*, a male snap prepared for dipping into the rubber emulsion (a similar female snap is shown attached to the original); *c*, the rubber mold prepared from the original, with slit through which the model was removed; *d* and *e* are halves of a furanose-ring mold (Figure 1*a*) cut apart to show the inside with female receptacles for the male snaps of original and copy; *f* and *g* are female and male snaps with anchors for holding to the plaster of the copy; *h*, the final single-piece plaster copy of the Cox model.

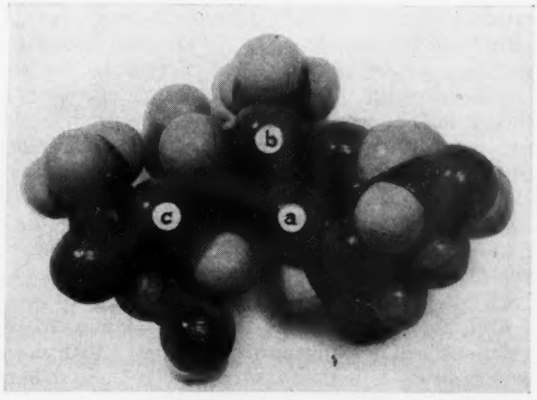
snaps have thread holes, thin wires can be inserted and twisted to form two wings extending from the snap, which should then be fairly rigidly fixed with respect to the wires. A continuation of these wire wings can serve to hang the snap or attached model during dipping later (see Figure 2*b*). Each snap is lightly predipped in the "liquid live rubber" emulsion which is in common use for making molds for plaster casting.

4. When dry the rubber-coated snaps are pressed onto the complementary fasteners of the model, covering all positions. Wing anchors are then trimmed to a convenient length, except for one which is left long for handling. The model is alternately dipped into the rubber emulsion and dried until the external snaps are well anchored and the model is covered by a rubber layer of about $^1/_8$-inch thickness. This will require four to six immersions over a period of about two days, depending on the fluidity of the emulsion. The thickness is chosen as a compromise between the desirable elasticity of a thin mold and the sturdiness of a thicker one. It is well to do the first half of the dippings with one side uppermost and then to hang the model upside down by the rubber "tail" thus developed for the remainder of the accumulation of rubber, in order to spread the coat more evenly. Finally all superfluous rubber appendages are cut off, and if time permits the rubber is allowed to dry for a day or so longer.

5. While it is customary in using rubber molds to make a plaster backing, most atom-model groups are small enough that a thick layer of rubber is able to support itself without significant distortion. Therefore, to prepare the mold for casting, one simply uses a razor blade to make a slit in the rubber, reaches inside with a knife blade, unsnaps the model from the mold, and removes the model. The position for the slit is chosen with regard to ease of filling with plaster, ease of unsnapping the copy from the mold after each casting, and the position where a seam will be least noticeable. Slits along atom edges are most often satisfactory, while slits across spherical atom surfaces leave unsightly marks in the copies and are to be avoided unless the mold is structurally weakened by any other cut. At some place along the slit a hole of about $^1/_4$-inch diameter is cut in the rubber for introduction of plaster. The final rubber mold appears as shown in Figure 2, parts *c* to *e*.

6. Preliminary to casting, a sufficient number of snaps are prepared for the copy by soldering to the back of each a bit of fairly stiff sheet metal (galvanized iron) bent into W- or V-shaped anchors (see Figures 2*f* and 2*g*). The mold is oiled on the inside with castor oil, the anchor-fitted snaps are inserted into the complementary receptacles in the mold, edges of the cut in the mold are fixed together by painting on a light coat of celluloid in acetone, and the mold is ready for the plaster.

7. A fairly good grade of white molding plaster is dusted into water until it begins to rise above the sur-



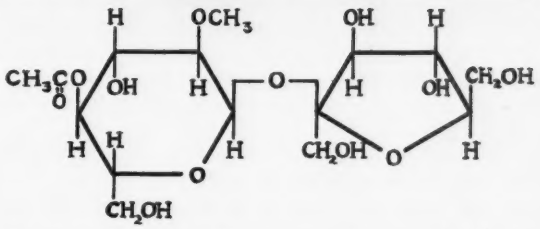


FIGURE 3.—MODEL OF A HYPOTHETICAL SUCROSE DERIVATIVE

The pyranose ring with its attached groups is on the left, the furanose half on the right. Bridging oxygen atoms are marked: *a* joins the hexose halves; *b* and *c* connect methyl and acetyl groups, respectively, with the glucose ring. The conventional formula below the photograph serves as a guide to the interpretation of the figure.

face; the mixture is stirred and run into the mold with care to prevent air bubble inclusion. After two or three hours the celluloid seams are stripped off and the finished cast removed from the mold. Excess plaster at the lip is easily cut off and, if necessary, imperfections can be remedied by painting or rubbing on a thin plaster paste. The final copy is typified by the one appearing in Figure 2*h*. Colored paints or enamels can be used to distinguish atoms of various types, a practice followed in preparing the groups of Figure 1.

To illustrate in a single molecular model the various types of application possible with these groups, Figure 3 shows a hypothetical derivative of sucrose. No attempt is made here to conclude anything regarding the overall dimensions and shape of this molecule, though it does appear that the pyranose and furanose rings, appearing to the left and right, respectively, can scarcely have their planes parallel because of congestion of attached groups in the neighborhood of the connecting oxygen atom, *a*. Bridging oxygens of the =O type are of use in two different ways in such models: as at *a* they join two hexose units, and in a similar fashion can be employed repeatedly for polysaccharide models; the oxygen atoms at *b* or *c* are used to attach methyl or acetyl groups and the like to positions occupied originally by the H atoms of the sugar OH groups.

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LECTURE EXPERIMENT ON THE SYNTHESIS AND COMBUSTION OF AMMONIA

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THE production of nitric acid by the arc process is a very common lecture experiment. But as the commercial production of nitric acid is now based on the oxidation of ammonia, it is desirable to show also the synthesis and combustion of ammonia in a lecture demonstration. It seems that such an experiment has not been described in the Anglo-American literature (*1*); hence, it may be worth while to give an account of the method used more than ten years ago in the Department of Technology at Königsberg (*2*).

For the synthesis of ammonia from the elements any source of hydrogen and nitrogen may be used. As the yield is not important, high pressure can be avoided, provided that a good tungsten catalyst is prepared. Following Franck's suggestions (*3*), 10 g. of purified, fibrous asbestos is soaked in a solution of 10 g. of tungstic acid in ammonia and evaporated to dryness. The dry asbestos is then heated to 600°C. in a hard glass tube in a current of dry ammonia gas, until the tungstate is reduced and the asbestos appears black. The catalyst is then cooled in a current of ammonia, and finally hydrogen gas is passed over it until ammonia can no longer be detected by the test with turmeric paper.

This catalyst is placed in a pyrex glass combustion tube supported horizontally and connected by a T-tube with two gas washing bottles and sources of hydrogen and nitrogen. The speed of the two gases through the wash bottles is regulated so that three bubbles of hydrogen enter the tube with one bubble of nitrogen. The issuing gases are led into an Erlenmeyer flask or other suitable receiver. As soon as the tube is free from any explosive mixture with air the catalyst is heated gently. After a short time the formation of ammonia can be shown in the receiver by the test with turmeric paper or the formation of white fumes of ammonium chloride.

For the combustion of ammonia the same apparatus may be used. The tungsten catalyst is replaced by platinized asbestos or platinum gauze. Ammonia gas and a mixture of two volumes of air and one volume of oxygen are passed at the same speed through the tube. The receiver contains a little water. As soon as the catalyst is heated to 400°C. it begins to glow without further heating and the formation of nitrous gases takes place. They dissolve readily in the water of the receiver where the presence of nitric acid can be shown by the usual tests.

Sometimes it happens that white fumes of ammonium nitrite are formed instead of the brown nitrogen dioxide. This is due to an excess of ammonia. In order to avoid this it is only necessary to reduce the quantity of ammonia passing through the tube.

In this form the oxidation of ammonia is less dangerous than the test tube experiment suggested by H. F. Davison (*4*). Moreover, it offers the advantage that the reaction is not stopped at the production of the nitrogen oxides, but is continued to the actual formation of nitric acid.

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Electrical Properties of Solids

Part II[1]

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AS PREPARATION for the treatment of the electrical properties of insulators, we shall first review the Debye theory of dispersion for liquids. Let us first consider a simple polar molecule such as chlorbenzene. The molecule is electrically neutral, and cannot dissociate into ions; consequently, it cannot carry a direct current. (The observed conductance of all ordinary liquids, with the single exception of water, is due to traces of electrolytic impurities.) The chlorbenzene molecule is, however, asymmetrical electrically: there is an excess negative charge density around the chlorine atom, which is balanced by an electron deficiency or an equivalent positive charge in the aromatic ring. In a D.C. field, an ion experiences a force which produces translation parallel to the field; a dipole experiences a torque, which causes rotation about the center of gravity of the molecule. Suppose we have a solution of chlorbenzene in benzene, dilute enough so that we may neglect interaction of molecular dipole fields and place it in a D.C. field. The field will tend to orient the dipolar parallel to the field. Opposing this orderly alignment, of course, we have the normal Brownian motion in the liquid; the dipoles are being constantly bombarded by solvent molecules, and as a consequence, no one dipole ever manages to retain any given orientation very long. But on a time average, taken over all the molecules, we will have a component of polarization parallel to the field given by

$$P = \frac{4\pi N}{3}\frac{\mu^2}{3kT}$$

where μ is the total moment of the molecule. If we turn the field off, the molecules will gradually assume a random orientation again; this does not occur instantaneously because it takes a finite time for a molecule to rotate in a viscous medium. The time required for the average orientation to drop to one e-th of its steady state value is called the time of relaxation, t. Since it is a measure of the time it takes for a molecule to rotate, we see that it is larger, the larger the molecule and the higher the viscosity of the medium. Also, since increased temperature means increased Brownian motion, *i. e.*, greater violence of thermal impact, we see that the orientation becomes random more quickly at higher temperature, other things remaining equal. Hence for t, we have

$$t \sim a^3\eta/T$$

Now if instead of a D.C. field, we apply an A.C. field across the electrodes, the polar molecules will tend to oscillate, first toward one electrode and then the other. If we assume that the period of the field is large (*i. e.*, low frequency) compared to t, the molecules will have ample time to follow the field, and we get a large displacement of charge in phase with the field. This corresponds to a high capacity current. We recall that a displacement of charge is sufficient for the production of an A.C. current. The current is at a maximum when the rate of displacement is a maximum; hence the A.C. current produced has maxima and minima where the applied A.C. field has zeros, because here the voltage is changing most rapidly. Consequently the capacitative current is 90° out of phase with the voltage. (An ionic current, on the other hand, is in phase with the voltage, because it corresponds to the motion of independent charges.) If we draw a vector diagram, we may represent the capacity current as a vector perpendicular to the voltage vector; reduced to unit volume, we may call the capacity current vector ϵ_0, the static dielectric constant. (We assumed very low frequency, so the capacity measured by the A.C. current is the same as the capacity which would be measured by the charge stored in the condenser by D.C.)

Now let us go to the other extreme from very low frequencies to very high, where the period is small compared to the time of relaxation. Then the molecule as a whole does not have time to rotate in the field; the viscous inertia of the medium is too great. Consequently, just as a D.C. galvanometer remains undeflected on account of mechanical inertia if an alternating E.M.F. is applied, the average position of a polar molecule is unaffected by a high frequency field, and the capacity current drops because we no longer get the charge displacement corresponding to dipole rotation. However, the electrons within the atoms of the molecule are still able to follow the field, and we obtain their displacement current. On the vector diagram, this corresponds to a vector ϵ_∞, the limiting value of the dielectric constant for very high frequencies. Numerically, it is equal to the square of the index of refraction.

Thus we see that polar materials exhibit high dielectric constants at low frequencies and low dielectric constants at high frequencies. The terms "high" and "low" are of course relative, and are reckoned with respect to the time of relaxation of the molecule: high frequency means $1/f \ll t$ and low frequency means $1/f \gg t$.

Let us now make a picture of what happens as we go from low to high frequency in the test condenser, holding the voltage (amplitude) constant. At low frequencies, as we have seen, the molecular orientation is in phase with the field, and at high frequencies, the di-

[1] Continued from J. CHEM. EDUC., **19**, 190 (1942). Lecture given at Brooklyn Polytechnic Institute, Brooklyn, New York, January 31, 1942.

poles pay no attention to the field. As the frequency is increased, the orientation begins to lag more and more behind the field because it has less and less time to adjust its motion to the alternating torque and reverse exactly in time with the field. If the orientation is no longer in phase with the voltage, the current vector is no longer perpendicular to the voltage vector, and it now acquires a component in phase with the voltage. This component is called the loss factor ϵ'', because it measures the electrical energy converted into heat per cycle. Obviously it will be at a maximum when the period of the field just matches the time of relaxation of the molecule. Therefore the current vector will trace a curve from ϵ_0 to ϵ_∞; on the basis of the Debye theory, this curve is a semicircle. Considered separately as function of frequency, the dielectric constant ϵ' follows an S-curve with ϵ_0 and ϵ_∞ as asymptotic values, and the loss factor ϵ'' goes through a maximum when $2\pi ft = 1$.

There is a simple electrical analog to the behavior of polar liquids. Suppose we consider a capacity ϵ_∞ parallel to a capacity

$$C = (\epsilon_0 - \epsilon_\infty)$$

in series with a resistance

$$R = t/(\epsilon_0 - \epsilon_\infty)$$

The admittance of the circuit is

$$\frac{1}{Z} = j\omega\epsilon_\infty + \frac{j\omega C}{1 + j\omega CR}$$

and the current for a voltage E is

$$I = E\left(j\omega\epsilon_\infty + \frac{j\omega CR}{1 + \omega^2C^2R^2} + \frac{\omega^2C^2R}{1 + \omega^2C^2R^2}\right)$$

$$= jE\omega\left(\epsilon_\infty + \frac{j\epsilon_0 - \epsilon_\infty}{1 + \omega^2t^2} - \frac{j(\epsilon_0 - \epsilon_\infty)\omega t}{1 + \omega^2t^2}\right)$$

If we write

$$\epsilon = \epsilon' - j\epsilon''$$

to summarize the composite circuit, we have

$$1/Z = j\omega\epsilon = j\epsilon'\omega + \epsilon''$$

and comparing the two equations, we have

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2t^2}$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\frac{\omega t}{1 + \omega^2t^2}$$

The two components of the current through the equivalent circuit are numerically equal to the dielectric constant and loss factor. If we imagine the condenser ϵ_∞ to represent the capacity due to electron polarization (which is always present) and C to represent the capacity due to dipole orientation in the absence of any friction, the resistance R appears as the drag on the molecules produced by the finite viscosity of the medium.

We now consider some of the consequences of the preceding theory. If we have a non-polar material, whether it be solid or liquid, we will have only ϵ_∞, the electronic polarization. Hence we will have a dielectric constant independent of frequency and equal to the square of the index of refraction, and zero loss factor on power absorption at all frequencies. The dielectric constant will decrease with increasing temperature, simply because there will be less matter per unit volume at higher temperature. These statements summarize the electrical properties of non-polar organic insulators. Inorganic insulators, such as quartz and Rochelle salt, are a little more complicated, if they are ionic. In these cases, a phenomenon known as the piezoelectric effect appears: compression or tension along the crystal axes produces surface charges, and conversely an alternating electric field produces periodic volume changes in the crystal. Space does not permit a discussion of this effect.

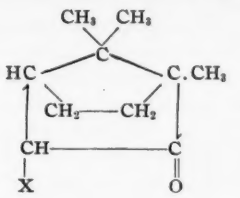
In the case of polar insulators, we expect to find a marked dependence of electrical properties on temperature, frequency, and molecular structure. According to the theory sketched above, we expect high dielectric constants and low losses when the frequency is small compared to $1/t$ and low dielectric constants and low losses when the frequency is large compared to $1/t$. The time of relaxation in turn depends on temperature in two ways: explicitly in the denominator, as a measure of thermal motion, and implicitly through the viscosity in the numerator. Since the viscosity decreases as an exponential function of (reciprocal absolute) temperature, the latter influence of temperature predominates. For a fixed frequency, we expect low dielectric constants at low temperatures, because the viscosity can become so high that dipole orientation becomes impossible, and then the dielectric constant will increase toward ϵ_0 as the temperature increases, and the decreasing viscosity permits orientation. When the dielectric constant goes through its sigmoid increase, we expect to find a maximum in the loss factor. All of these general predictions have been verified by experimental work on polar liquids.

With this as the background, let us now turn to a consideration of polar solid insulators. The simplest is produced by the freezing of a polar liquid. In general, when the molecules lose their freedom of translational motion and assume the lattice points characteristic of the crystal, they also lose their freedom of rotational motion, and we have an abrupt drop from a high dielectric constant to a low one, because dipole orientation is no longer possible if the molecule cannot rotate.

One important group of exceptions must be noted, however. Pauling in 1930 suggested that hydrogen halide molecules might rotate in the solid. Experiments verified this prediction, and since then a number of crystalline substances have been found which show high dielectric constants in the solid phase, below the melting point. At still lower temperatures, the rotational degrees of freedom freeze in, and here the dielectric constant drops to its optical value. The dielectric constant–temperature curve is *continuous* through the melting point.

Camphor, for example, freezes at 175°, at which temperature the dielectric constant is about 7. Its

polarity is due to a ketone group. A continuous curve from higher temperatures goes through this point, rising to about 15 at −40° where the dielectric constant suddenly drops to 2.6, the optical value, and then remains practically independent of temperature. On heating, there is some hysteresis; at −30°, the dielectric constant suddenly increases to about 13, and on further heating the curve merges into the one obtained on cooling. Camphor derivatives show a similar behavior.



Camphor has a structure which gives it an approximate spherical symmetry. And one property of spherical molecules is that they have very small van der Waals force fields; *i. e.*, it is easy to rotate them. Hence, even in the solid state, the camphor molecule will rotate. If a chlorine is substituted at X in the formula, rotation begins at 75°; that is, it takes more energy to rotate chlorcamphor, because it is lopsided. A bromine at X completely inhibits rotation in the solid state, and the compound does not show a high dielectric constant until it melts. The freezing-in of rotation for these molecules is abrupt: the drop in dielectric constant is independent of frequency below 100,000 cycles.

Another group of polar solids, also investigated in the Bell Laboratories, shows a somewhat different behavior. These are the completely substituted benzenes. A chlorine atom and a methyl group have about the same volume. By different combinations, eight different polar hexasubstituted chlormethyl benzenes can be made. All of these show high dielectric constants in the solid phase, but unlike the camphor derivatives, the dielectric constant at a given frequency drops off over a temperature range. The inflection point comes at different temperatures for different frequencies, showing that here we have a real dispersion. In contradistinction to the camphor derivatives, these molecules are disc-like rather than spherical, and in the crystal lattice rotation in the plane of the disc appears to be possible over a wide range of temperatures, but the resistance to rotation increases with decreasing temperature. Hence, just as in the case of polar liquids of increasing viscosity, we must go to lower and lower frequencies as the relaxation time increases in order to find high dielectric constants.

Finally we turn to a consideration of polar polymers. Data for a typical polar polymer, polyvinyl acetate, show a superficial resemblance to the properties of polar liquids: with increasing temperature, the dielectric constant increases from a low value to a limiting value independent of frequency and dependent only upon temperature, and the loss factor goes through a corresponding maximum. This similarity at once leads to the hypothesis that linear polymers behave internally (that is, as far as molecular motion is concerned) as liquids of high viscosity. The dispersion range is in the audio frequency band for most linear polymers, especially at moderate or high temperatures and for plasticized polymers such as polyvinyl chloride. This means relaxation times of the order of milliseconds, as compared with times of the order of 10^{-8} to 10^{-10} seconds in ordinary liquids. A longer relaxation time means a higher viscosity or a larger molecule; in the polymers, probably both influences are operative. The whole effect can, of course, not be due to the high molecular weight of the polymer, because it is inconceivable that the whole polymer molecule can rotate as a unit; it is too big and too flexible. But large segments of the molecule can on a time average act as a single unit. Nevertheless, the large relaxation times in the polymers seem most probably due to a high internal viscosity. This viscosity need not be the macroscopic viscosity of the plastic, of course; in fact, although high, it is probably much smaller than the viscosity derived from measurements on a sample of the plastic in bulk. By "internal viscosity," we mean here simply the coefficient describing the resistance to molecular motion, and *a priori*, we have no reason to assume it equal to the bulk constant, although we may reasonably expect a correlation.

Aside from the frequency range in which dispersion occurs for polar polymers, there are other significant differences between their properties and those of simple polar liquids of low molecular weight. The most striking difference is in the shape of the E' and E'' frequency curves. According to the Debye theory, the height of the loss factor maximum should equal exactly half the difference between the static and optical dielectric constants, and most of the dispersion and absorption should take place within a few decades of frequency. Instead, in the polymers,

$$E'' \text{ max} < (E_0 - E_\infty)/2$$

and the dispersion range is many decades wide. An explanation for this behavior can be found in the structure of the polymer. In the monomer, each molecule is mechanically independent of its neighbors, and can be characterized by a time of relaxation which is the same for all the molecules. But the dipoles in a polar polymer are tied by primary valence bonds to other dipoles. Hence the motion of any one dipole and its orientation are influenced by and influence the motion of other dipoles in the same molecule. Furthermore, each chain molecule can assume a number of different configurations, each with a characteristic moment and effective size, and in these different configurations, various segments of the molecule, which act as units in the electric field, will assume many orientations. The many degrees of freedom of the flexible chain molecule permit many ways in which rotational diffusion can take place to bring about equilibrium in the field, each characterized by a different diffusion constant and relaxation time. The net effect of the chain structure is thus

to produce a distribution of relaxation times, and the obvious result of this on the electrical properties is to broaden the dispersion region—instead of a single peak, we have the resultant of many superimposed peaks. Detailed calculations have shown that it is possible to account for the electrical properties of polar polymers using this model.

Another consequence of chain structure should be mentioned. In general, polar polymers have much higher static dielectric constants than the corresponding monomers. For example, ethyl chloracetate has a dielectric constant of 10.5, while the corresponding polymer, polyvinyl chloracetate, has a static dielectric constant of 25. Similarly, the dielectric constant of ethyl chloride at the critical point is about 5, while E_0 for polyvinyl chloride is 13. In the monomeric liquid, each dipole is free to rotate independently—they rotate not only in external fields, but also under the influence of each other's fields. The latter orientation leads to many configurations in which dipole moments cancel each other pairwise by antiparallel alignment, and hence are not available for orientation by an external field, and likewise are unable to contribute to the dielectric constant. Indeed, if it were not for this association, the dielectric constants of ordinary liquids would be of the order of thousands, instead of having a maximum value of about 100. In the polymers, the dipoles are tied to the carbon chain, and while they retain considerable freedom of rotation, due to the flexibility of the chain, they do not have any independent translational freedom. Consequently, we get mutual cancellation of moments only when it is permitted by the convolutions of the polymeric chain, and this happens less frequently in the polymers than in the case where the dipoles are on mechanically independent molecules. Therefore, we expect and find higher static dielectric constants in polar polymers than in the corresponding monomers, assuming that the temperature is high enough to permit orientation.

The low temperature behavior of many polymers is also different from that exhibited by systems of low molecular weight on cooling. If we cool a polymer from the temperature at which, say, the 60-cycle absorption shows its maximum, we find at first a rapid decrease of dielectric constant and loss factor. Then at a fairly well-defined temperature (within several degrees), the rate of decrease of E' and E'' suddenly decreases very markedly. Instead of proceeding asymptotically to zero, the loss factor goes through another maximum, much broader than the high temperature dipole peak. The dielectric constant slows down to a linear decrease, and it is obvious from the data on hand that a very wide temperature range is needed before the dielectric constant will drop to the optical value. The abrupt change in the gradients of the electrical properties is accompanied by a significant change in mechanical properties. Above the critical temperature range, the plastic is elastic—it elongates under an increasing tensile load, much like a piece of rubber, before it breaks. Below the critical range, the plastic is brittle. It remains nearly unchanged in length under an increasing tensile load, and then suddenly snaps. The change in mechanical and electrical properties seems to find its explanation in a partial crystallization which occurs at the transition temperature. At high temperatures, the plastic behaves internally like a liquid, as has already been said. At the critical temperature, local crystallization begins, and much of the rotational freedom is frozen in. On account of the large size of the polymer molecules and the large values of the times of elastic relaxation, this crystallization cannot proceed uniformly as in the case of compounds of low molecular weight, but can occur only over small regions, to give tiny crystallites in which the chains are properly oriented, separated by amorphous regions in which geometry prohibits crystallization. These regions are thermodynamically unstable, in that there is in principle a state of lower energy, but the viscosity is so high that the amorphous region is preserved in a configuration characteristic of a higher temperature. That the low temperature maximum in absorption is due to chain-chain interaction is clearly shown by the fact that the addition of relatively small amounts of a substance of low molecular weight (plasticizer) will eliminate the maximum. Also, polymethylacrylate shows a low temperature maximum, while polymethylmethacrylate does not. In the latter case, the methyl group on the same carbon as the polar group probably interferes with proper close packing of the chains and thus prevents alignment and crystallization.

The general behavior of the polar polymer–plasticizer system can be completely explained in terms of the model already described. We assume a distribution of polar groups along the carbon skeleton of the chain molecule, and describe their response to an external field by a distribution of relaxation times which depends on the average chain length. If the temperature is high enough and the frequency low, we get maximum response of the dipoles, with low power absorption. As the temperature is decreased or the frequency increased, the dielectric constant decreases, and the loss factor goes through a maximum.

The plasticizer gives us another independent variable which may be used to control the relaxation time. At a given temperature, the presence of increasing amounts of plasticizer lowers the internal viscosity, and we get a corresponding shift of maximum absorption to higher frequencies.

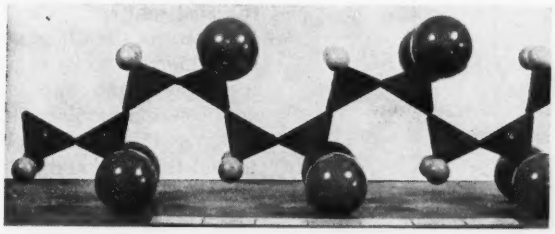
Experimental studies have shown that the polymer–plasticizer relationships are very analogous to solvent–solute relationships. For a polar polymer, it is necessary that the plasticizer be polar, or at least polarizable; thus petroleum ether merely wets polyvinyl chloride, while diethyl ether and aromatic hydrocarbons swell it. The vapor pressure of diphenyl over PViCl–Ph_2 plastics is much less than the vapor pressure of diphenyl at the same temperature, which indicates a high interaction. Amyl naphthalene, on the other hand, is a poor plasticizer. Weight for weight, a plasticizer of low

molecular weight is more effective in reducing internal viscosity than a plasticizer of high molecular weight. This clearly indicates that plasticization is a local interaction between the added molecule and part of the polymeric chain, and is more effective the more places the chains are separated or uncoiled.

When we come to the thermosetting polymers, such as bakelite, we find a different situation. Here the absorption is not very sensitive to temperature and covers an extremely broad band of frequency. The cross linking provides a much wider range of relaxation times than is possible in the linear polymers, and we probably also have absorption, particularly at high frequencies, due to isolated hydroxyl groups which did not enter the condensation reaction. Jackson made some very pretty experiments in which he showed the possibilities of different mechanisms of absorption for a given substance. For example, when β-naphthol is dissolved in polystyrene, and the loss at one megacycle as a function of temperature is measured, two peaks in absorption appear. The low temperature one is ascribed to the motion of the hydroxyl groups with respect to the aromatic nucleus, while the high temperature one is assumed to be due to rotation of the whole naphthol molecule. Since polar groups are necessary for the phenol-formaldehyde and similar condensations, and since it is highly improbable that all reactive groups will find reaction partners, it seems unlikely that cross-linked, loss-free polymers can ever be obtained. The only exception is in the case of the ethylenic bond; divinyl benzene, for example, can cross-link styrene to give insoluble resins, which, being hydrocarbons, are substantially loss-free.

There is a very interesting parallel between the polarity of the groups in a polymer and its other properties. Suppose for the moment we consider all polymers as linear, with various sorts of cross bonds. In polythene and polyisobutylene, we have the weakest possible sort of cross bonding. The polymers are waxy or soft solids, with little elasticity or tensile strength. Also, they are completely non-polar. Next, we have natural rubber, where, due to the polarizability of the ethylenic double bonds, we have higher mutual van der Waals forces and greater elasticity and tensile strength. The benzene ring is more polarizable than the ethylenic bond, and correspondingly, polystyrene is hard at room temperatures and elastic only at elevated temperatures. So far, we have considered cross bonds due only to induced dipoles in polarizable groups. In the synthetic rubbers, Buna S and Buna N, we have first ethylenic polarizability of the butadiene groups, and superimposed on this, the stronger attraction of the benzene rings or the nitrile groups. Buna S is a good insulator, with low losses, while Buna N is a poor dielectric, on account of absorption due to the polar nitrile groups (and also to conducting impurities, possibly arising from partial hydrolysis of the nitrile groups). In the next state of polarity, we have the polyhalides and polyesters. These are usually hard and brittle up to quite high temperatures and can only be softened at room temperature by the addition of a swelling agent. A still more intense form of cross bonding appears in cellulose and silk, where we have strong hydrogen bonding. These materials are not thermoplastic at all and can be molded only by the addition of a swelling agent. (This may be done internally, as in the nitration or acylation of cellulose; masking the hydroxyls eliminates some hydrogen bonds, and we again obtain thermoplastic materials.) Finally, we reach the stage of covalent cross bonding. A mild degree of cross bonding, as in soft vulcanized rubber, leaves some elasticity in the plastic, but if we have many cross bonds, as in bakelite, urea-formaldehyde, melamine resins, and the like, the material has no thermoplasticity whatsoever. At the end of the list is diamond, which is the ideal case of a completely covalent cross-bonded polymer.

FORMULA OF THE MONTH



Courtesy of Industrial and Engineering Chemistry

STRUCTURAL FORMULA FOR POLYVINYLIDENE CHLORIDE

$(-CH_2-CCl_2-CH_2-CCl_2-)$

Showing two units of the polymer which composes the plastic known by the trade name of "Saran."

A DEVICE TO DEMONSTRATE ELECTRONIC TRANSFER IN REDOX REACTIONS

LUIS F. LEROY

University of Havana, Havana, Cuba

THE apparatus set up to demonstrate the electronic transfer in redox reactions usually consists of two beakers containing the oxidizing and reducing solutions, respectively, connected across a "salt bridge." The latter is a solution of any electrolyte having no chemical action with either the oxidant or reductant, and intended only to close the circuit so that the electrons may flow when the two solutions are connected by means of a conductor.

By this salt bridge device, the rate of redox reactions may be so retarded as to render visible certain intermediate steps that would otherwise pass unobserved. An instance is the reaction between stannite ions and bismuth nitrate. Carried out in test tubes, the intermediate formation of the basic salts or of bismuth hydroxide is scarcely visible, unless the stannite solution is diluted and added very slowly to the other solution. Usually the formation of the black precipitate of metallic bismuth is the only reaction observed. With the salt bridge device, on the other hand, the primary steps are clearly seen.

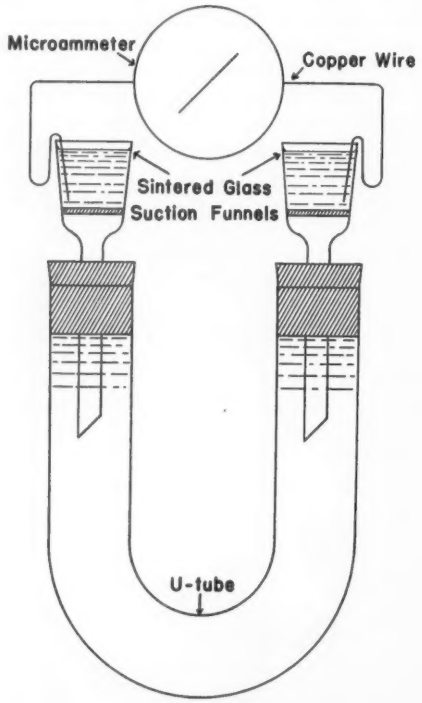


FIGURE 1

The device (Figure 1) consists of a U-tube about $^3/_4$" in diameter filled to the top with a 10 per cent NaCl solution, or 6 *M* HCl. Two sintered glass suction funnels are attached by rubber stoppers to the U-tube. The space between the end of the funnel and the lower face of the porous plate is filled with the same electrolyte as that contained in the U-tube. This is easily accomplished by means of a pipet, but care should be taken that no air bubbles are formed while inserting the funnels, since this increases the resistance of the salt bridge. The external circuit consists of two copper ribbons or thick copper wires dipped into the solutions of the oxidant and of the reductant which are placed in the funnels, and connected in series across a microammeter. If the scale of the microammeter is too low, the current through it may be reduced by use of a shunt.

Practically any redox reaction serves well for the purpose of demonstration. A 0.0002 *M* solution of $KMnO_4$ with dilute sulfuric acid placed in one cup is readily decolorized within an hour by a moderately concentrated solution of $SnCl_2$ placed in the other. A current as high as 250–300 microamperes is seen to flow across the meter, going from the oxidant to the reductant when 6 *M* HCl solution is used in the bridge.

Using the same electrolyte as in the preceding case and dipping a copper plate in 6 *M* HCl in one cup, and in the other one a carbon or platinum electrode in dilute nitric acid, it will be observed, when the circuit is closed, that a current is flowing from the nitric acid solution to the copper plate; in an hour the blue color due to the cupric ions will be observable in the HCl solution, before which the specific test for copper with ammonia solution will yield positive results.

The reaction between iodide ions and dichromate ions is readily performed in the apparatus described. Within an hour, a brown color due to the iodine liberated is perfectly visible, and shortly thereafter a change from yellow to pale green is observed in the other cup. The inverse reaction, the decoloration of iodine solution by thiosulfate ions, can also be accomplished, but the solution in the bridge cannot be acid as it would decompose the thiosulfate solution. A 10 per cent solution of sodium chloride can be used for this purpose.

An interesting redox reaction which can be studied is the action of stannite ions upon bismuth nitrate, in nitric acid solution. This reaction is interesting because it illustrates the different values of electroaffinity with two different oxidants. When the circuit is closed a white precipitate appears in a few hours in the nitric acid solution of bismuth ions, owing to the fact that $NO_3^- + H^+$ has a much higher normal oxidation potential than the normal oxidation potential of Bi^{+++}; and the electrons given up by the SnO_2^{--} ions are easily taken up by the $NO_3^- + H^+$ rather than by the Bi^{+++} ions. When this occurs bismuthyl nitrate precipitates according to the reaction

$$Bi^{+++} + 2NO_3^- + 2H^+ \longrightarrow H_2O + NO + BiONO_3\downarrow$$
$$\uparrow + 3\epsilon$$

A Method of Teaching Thermodynamic Functions[1]

HAROLD BECHER *Polytechnic Institute of Brooklyn, Brooklyn, New York*

IN TEACHING beginners in physical chemistry or chemical thermodynamics, difficulty is often encountered in making the student visualize the relationships between thermodynamic functions such as

$$\Delta H = \Delta F + T\Delta S$$

or

$$F = A + PV$$

Particularly, it has been found that in the Lewis and Randall notation, trouble is found in defining ΔH or $-\Delta H$.

However, from several years' experience, it has been found that the subject matter is readily visualized by means of the accompanying simple diagrams.

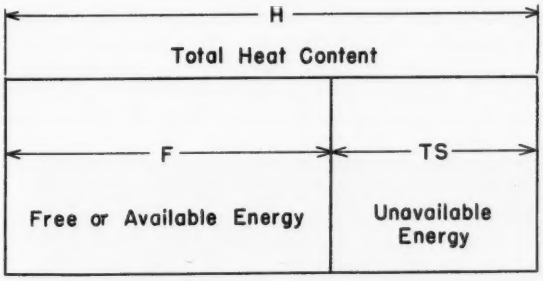


FIGURE 1

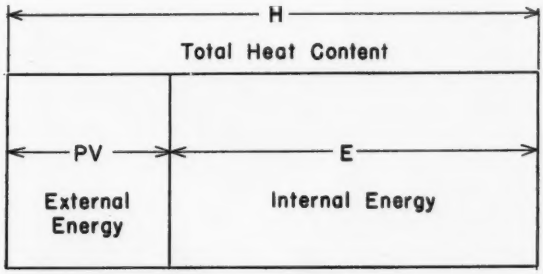


FIGURE 2

Each rectangle represents a thermodynamically isolated isothermal system in which

H = Heat content or total energy
PV = Pressure-volume content or available external energy
F = Free energy content or available energy
A = Work content
E = Internal energy content
S = Entropy content
n = Valence
T = Absolute temperature

[1] Presented before the Division of Chemical Education at the 102nd meeting of the A. C. S., Atlantic City, New Jersey, September 11, 1941.

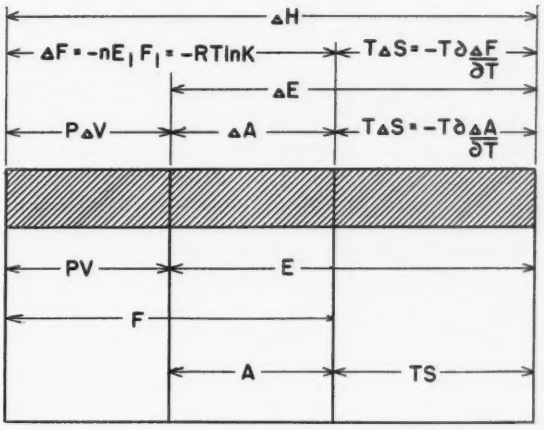


FIGURE 3

TS = Unavailable energy
F_1 = Faraday
E_1 = Voltage

From an inspection of the diagrams it becomes obvious that if heat is evolved, H, the total heat content, is diminished by a quantity $-\Delta H$, and if heat is absorbed H is increased by ΔH. This increase or decrease is indicated by the shaded portion of the rectangle (Figure 3) and the notations above it. The same idea follows for the other functions.

The relationship between A and F is at once clear from Figure 3. The Gibbs-Helmholtz equation is derived by differentiating

$$\Delta H = \Delta F + T\Delta S$$

or

$$\Delta E = \Delta A + T\Delta S$$

(the latter at constant volume), obtaining the relationship

$$T\Delta S = -T\partial\Delta A/\partial T$$

or

$$T\Delta S = -T\partial\Delta F/\partial T$$

The connection between the last two relations and the electrochemical function nE_1F_1 becomes clearer when referred to Figure 3.

When the diagram is explained to the class at the very beginning of the course the further study of thermodynamics is facilitated. The first law

$$\Delta H = \Delta E + P\Delta V$$

is grasped at once. Particularly is this so if heat is at first represented (although incorrectly) as a fluid. This

is advisable as an aid in visualizing the functions. The heat transfer into or from the system becomes analogous to transferring a quantity of liquid from a pitcher into a glass. The liquid fills the glass to the limit of its capacity and overflows into the space surrounding it. Likewise, heat from an external source can enter the system, increasing its internal energy to the limit of its capacity, and the excess will increase the pressure-volume content, or, in other words, do work. This last is analogous to the water which overflows the glass.

PHASE MODELS FOR TERNARY SYSTEMS

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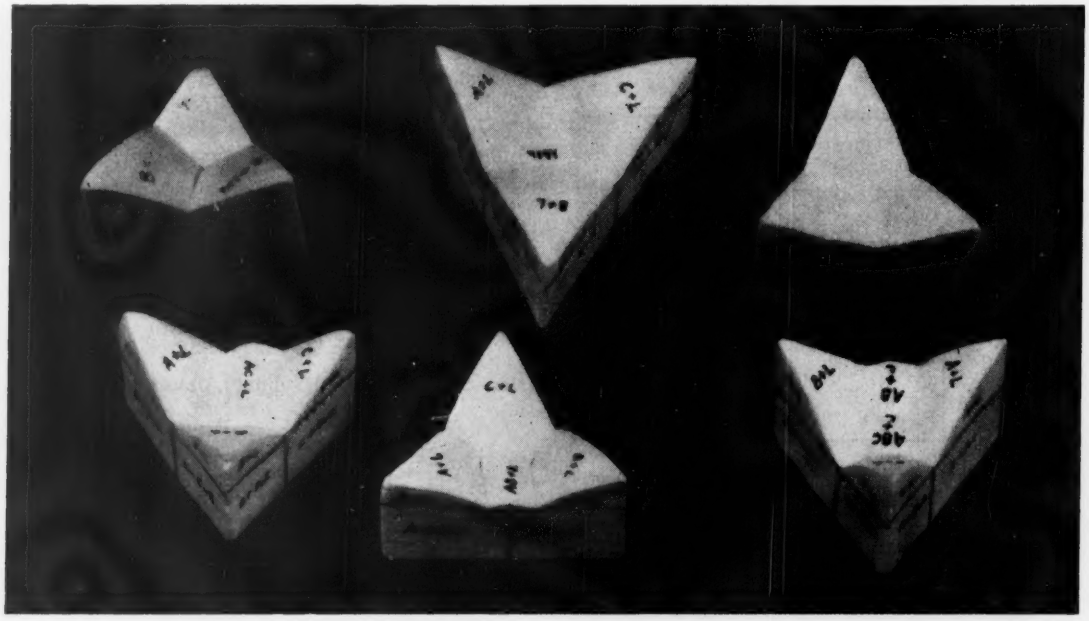
THE teaching of heterogeneous equilibria and the phase rule is ordinarily difficult because the highly important ternary systems require the use of three-dimensional models. Thus, a great portion of the time allotted to class discussion of such systems must be given to the purely geometrical problem of passing from a conventional, plan-view, triangular figure to the completed equilibrium surface in space. This limits the opportunity for dealing with the significant, and often complicated, aspects of their physical and chemical behavior. This is a problem which should not be treated too lightly, for the student must be able to make such transitions with sureness and ease in order to apply his previous knowledge of binary systems. The author has felt that the models now on the market do not sufficiently stimulate the powers of visualization, and has required students to carve phase models out of soap, working only from printed, two-dimensional diagrams. The experiment has been so successful that we have adopted it as a regular assignment in one of our courses of physical chemistry.

The project extended over a period of two weeks and consisted of preparing the space analogs of the six typical concentration–temperature diagrams of Rankin and Wright,[1] a choice dictated by the fact that the students concerned were majoring in ceramic or geological engineering. The work was carried on in pairs, and large half cakes of Ivory soap were used. The accompanying photograph shows a typical set of models.

Acquiring a general familiarity with the space relation of ternary diagrams is ordinarily difficult. In this work, after lettering his models, the student clearly perceives their connection with the binary cases. In a manner far more effective than by mere discussion, he is aided in comprehending the differences between alteration lines and eutectic lines, hesitation points and quintuple points, etc. Further, the models can be saved from year to year, and the student can turn to them for review when he must apply his knowledge of these systems.



PHASE MODELS CARVED IN SOAP

[1] RANKIN AND WRIGHT, "The ternary system CaO–Al_2O_3–SiO_2," *Am. J. Sci.*, **39**, 18 (1915).

High-School Chemistry

Liquid Glass and Solid Solutions

C. H. JEGLUM *Philadelphia Quartz Company, Philadelphia, Pennsylvania*

ON A rocky little peninsula that juts out a few hundred yards into the cold waters of the Atlantic stood a boy and his father looking back across a pocket of the sea to Bald Cliff, which rises straight as a wall, ninety feet above the water's edge. A few minutes before they had stood on the top of the cliff, felt the spray on their cheeks, and heard the rhythmical thunder of the surf as the great rollers broke against its face. Now, after scrambling down a narrow trail to the foot of the cliff, they could see the glossy redness of the massive rock that formed this spectacular bit of rugged New England coast.

"Dad, why is there nothing but rock here while on the Jersey coast there is only fine white sand?" queried the lad.

His father was startled, for in that question he heard his own voice as twenty years earlier he had stood at this same spot and wondered similarly.

"It may be a matter of age, son. The Jersey coast is very, very old, while in this area the upheavals of earth which have bared these huge rocks may have taken place much more recently, not within our life span, of course, but rather as time is reckoned geologically. Sand is nothing but bits of rock formed by the eternal pounding of wind and water against such apparently resistant surfaces as these. You have felt the sting of sand hurled at your body when you played on the beach on a windy day, and you have seen grimy office buildings cleaned by blowing a jet of sand against the granite with sufficient force to cut off a thin outer layer of stone. Nature does the same thing on these rock walls. Ice, too, disintegrates the rock. Water seeps into crevices, and when it freezes the expansion develops tremendous forces which split the big rocks into smaller ones. The waves tumble one rock against another. Slowly but steadily the work goes on until finally we no longer have great rocks. Only the sand remains.

"And even the sand particles themselves change. Do you recall the time we examined the sand from a deposit near Ottawa, Illinois, and compared it with sand we had brought from the beach at Atlantic City, New Jersey? The two looked alike in color, but under a big magnifying glass we could see that the specimen from the ocean shore had many sharp edges. The particles were too small to cut your feet as you ran on the beach but the edges were really jagged and sharp compared with the Ottawa sand which was round and smooth, like irregular spheres. That Ottawa sand had been blown about by the winds for such a long time that the rough edges were all knocked off and the spheres had acquired a polish which gave it luster and brilliance. Wind worn sands are often more uniformly spherical than the water worn sands of the sea shore."

The boy's interest in silica was satisfied for the time being, but let us continue the story.

Chemically the Ottawa and New Jersey sands are very similar. Each will run over 99 per cent silica (which is SiO_2, the oxide of silicon), and the remaining one per cent is made up of the oxides of calcium, magnesium, aluminum, zirconium, titanium, and iron which happened to be present in the solution at the time the hydrated silica dropped out of the waters which had been carrying it. Of course all sands do not run so high in silica; many contain much less, but almost any sand you find will carry over 90 per cent.

Sand is not the only source of silica. You will encounter it elsewhere in great quantity: in the rocks, in the soil. Indeed, according to estimates of geologists, almost three-fifths of the entire earth's crust is composed of silica. Anyone who has traversed the great desert of our Southwest will not be surprised at such a statement, but those acquainted only with the rich black loam of Iowa or Illinois may wonder. However, even these soils which are not ordinarily considered "sandy," will contain 70 per cent or more of SiO_2.

Natural waters, too, carry silica, often in amounts of only three or four parts per million, although sometimes, as in the hot springs of the Yellowstone, there may be present several hundred parts per million of silica.

Even in the vegetable world silica is to be found. The seed hulls of rice contain about 35 per cent. The familiar equisetum or horsetail rush which grows along the banks of streams where it can get its feet in the water carries so much silica that Boy Scouts find it an excellent agent for scouring their cooking utensils. Some desert plants contain a great deal of silica. "Spanish Dagger," for instance, has such a stiff skeleton from the large amount of silica it contains that cowboys have used it in lieu of a knife for slashing a horse's leg to induce bleeding after an encounter with a rattlesnake.

A plant which is very common, and yet one which few people ever see, is the diatom. This is a microscopic, single-celled plant present in almost all waters, including those you drink. Although it is very tiny the diatom is an important food source in the economy of nature, particularly in relation to sea animals. It can convert carbon dioxide into carbonaceous foods by utilizing light, a process known as photosynthesis. Animals cannot do this, and as a result, the diatom is the primary source of food for many tiny aquatic animals which in turn are eaten by the larger animals.

Even the Arctic whale is thus dependent on the diatom.

Our particular interest in this curious plant is that it picks up silica from the water and builds it into its

Courtesy of the Johns-Manville Research Laboratories

DIATOM SKELETONS RECOVERED FROM BEDS OF DIATOMACEOUS EARTH; USED FOR FILTER AID

skeleton to form little pillbox-shaped bodies, beautifully patterned in amazingly complex fashion. There are thousands of varieties of these diatoms and when viewed through a microscope, particularly with polarized light, the colors and patterns are strikingly lovely. When the diatom dies the organic envelope around the skeleton disintegrates, but the silica framework itself remains and settles to the floor of the sea. In some areas, as at Lompoc, California, the ocean waters have receded, exposing beds more than a quarter of a mile deep and five square miles in area composed entirely of these diatom skeletons. At the rate of fifty million diatoms to a cubic inch, how many did it take to form this vast deposit? And if, as is believed, a half-inch layer of these skeletons settled to the bottom every year how many thousands of years did it take to form this great bed?

Deposits such as this are not unlike fine sandstone in appearance but the microscope will reveal its true origin. The material is valuable commercially, particularly as an aid to filtering solutions such as those of sugar or fruit juice. The silica skeletons pile up on the filter plate to form a porous mat which does not readily clog but is remarkably efficient in removing the tiny particles from cloudy solutions to yield brilliant and sparkling fluids.

But let us return to silica itself. What is it like?

Silica is not very active chemically. Only hydrofluoric acid will dissolve it at ordinary temperature but if it is combined with a flux like sodium carbonate and heated to about 1300°C. a remarkable thing happens. The silica dissolves completely and when the mass cools a beautiful, clear glass remains. It may be deep green or brown or almost blue depending on the amount of iron or other impurities which were present in the silica, but if fusion has been complete the glass will be clear enough to permit newsprint to be read through a piece two or three inches thick.

If you hit this glass with a hammer it will break with a shell-like (conchoidal) fracture characteristic of all glasses. Its edges are sharp enough to cut your hand. But in one way it does not behave like the glass which you normally encounter in your home. If you put a little of it in water and add a drop of phenolphthalein you will see the solution slowly become wine red, showing that the glass is dissolving. But don't be too sure. You may stir this for days, you may heat it to boiling, but beyond a little surface solution it doesn't dissolve much further. Perhaps, after all, it is the same as window glass.

Let us try one more test. Let us pulverize the glass, then put it into a pressure cooker with only a little water and heat it at about twenty pounds pressure for an hour. This time you will find it has truly dissolved. Ordinary window glass won't do that. The glass formed from soda ash and sand, then, is definitely soluble. For that reason it is often called "water glass."

Examine the solution you have formed. You will notice immediately that it is thick, viscous, sticky. Add a little hot water. The viscous mass thins out nicely. Add a little acid. There is an immediate precipitation of gelatinous silica which will not go back into solution even if the acid is neutralized.

The curious material we have made is a silicate of soda. It differs from ordinary glass in that it contains no lime. During the fusion of alkali and silica the carbon dioxide split off from the sodium carbonate and escaped as a gas. The alkali combined with the soda according to the following simple equation:

$$Na_2CO_3 + XSiO_2 \rightarrow Na_2O{\cdot}XSiO_2 + CO_2$$

Theoretically any proportion of silica to soda could be used. Practically, furnace combinations are limited to a maximum of four parts SiO_2 to one of Na_2O. The exact amount depends on the use to which the silicate is to be put, for as the proportion of silica to soda changes, markedly different properties are obtained.

The most silicious of the commercial silicates, $Na_2O{\cdot}4SiO_2$, is about as thick as maple sirup and just about as sticky. If an attempt is made to concentrate it by boiling off a little water it thickens and becomes rubbery. It can be crumbled in the hands and pieces of it bounce in lively fashion.

If we go to the other extreme we can make a solution with only 1.6 times as much silica as soda ($Na_2O{\cdot}1.6SiO_2$). This can be concentrated so that it contains just about twice as much total solids (alkali and silica) as the 1:4 variety. At this high concentration it looks like a solid, but lay a piece across two supports and after a time you will see that the center has sagged a little. That will prove to you that it is still a solution. If you grasp a piece of this "solution" between your two hands and give a sharp tug you will find that it

stretches to arm's length and can be "pulled" like taffy. It is very sticky so don't get it in your hair, but if you do a hot shower will wash it away. It is quite unlike the stickiness of chewing gum in that respect.

Between the highly silicious silicates and the highly alkaline ones, there are many others which are regular articles of commerce. Most of them are liquids but some are powders. The glass is sometimes crushed to a fine white powder, or the liquid may be squirted through a nozzle and the tiny droplets dried by a blast of warm air to form little beads which are soluble, even in cold water.

What are these strange, sticky fluids good for? Who could make use of a glass or powder which will dissolve so slowly?

Surprisingly enough the silicates have a great many uses, some of them of much commercial importance. Indeed, industry consumes the equivalent of more than ten thousand carloads of silicate each year.

There are many chemicals such as sulfuric acid, chlorine, and caustic soda, which are almost unknown to the layman but which, nevertheless, are necessary to his comfort. Without them he would not have the plastics, cellophanes, lacquers, rayons, and synthetic rubbers which are so much a part of our daily requirements. The silicates of soda are similarly unknown to the layman but nevertheless he is dependent on them for many things.

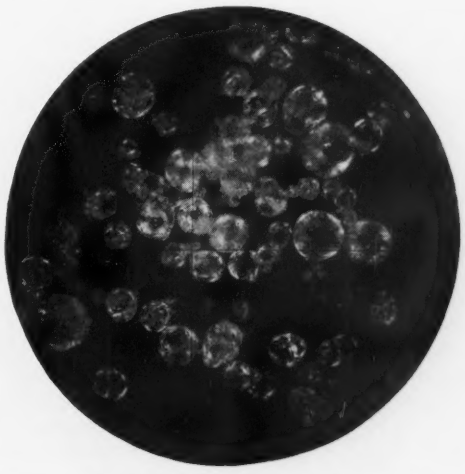
Did you ever examine a corrugated paper box? Pick up the one nearest to you and look at it closely. You will see that it is made up of three sheets of paper, the center layer of which is corrugated. Try to separate the three layers. If the board is well made you will have difficulty but you may be able to expose a part of the glue line which will probably appear as a glossy, shiny film. Moisten it with water and add a drop of phenolphthalein indicator. Very likely you will see a pink line develop, which is evidence that the adhesive is an alkali, a silicate of soda. This use, the combining of paper to make board is one which takes tons and tons of silicate each year. If you stop to recall that practically everything, from such heavy objects as refrigerators and gas ranges to fragile glass and china, is shipped in cases made from paper board it will help you to realize how dependent we are on these strong, lightweight shipping cartons.

The machines which make this board are fascinating to watch. The sheet to be corrugated, usually made from straw, is steamed to soften it, then run between grooved metal rollers to form the corrugations. The tips of the corrugations are coated with silicate of soda applied by a roll revolving in the adhesive pan, the liner sheet is brought up in contact with it, and from above the other liner is brought into position. The formed sheet passes next over a series of hot plates which dry the adhesive. Then the board passes through a knife built like a guillotine, which travels forward with the sheet to prevent it from buckling as it is neatly sliced to the required size.

Machines of this sort turn out three miles of board every hour and for such speed it is obvious that the adhesive must be carefully designed to wet the paper, soak into it just the right amount, and to change from a liquid to a semisolid (that is, to take its "set"), at just the right instant. The silicate which has about three parts of silica to one of soda meets these requirements. A more silicious grade would set too fast, a more alkaline one too slowly.

Do you occasionally (or perhaps all too frequently) take your turn at the sink in washing the supper dishes? In that operation you very likely use silicate of soda, for kitchen soaps, be they bar or powder, contain generous quantities and for a very good reason. Soap manufacturers have learned by careful laboratory study that silicate greatly increases the cleansing ability of pure soap. Washing is really a combination of several processes. First, the dirt to be removed must be thoroughly wetted. Water by itself wets most surfaces very slowly but the action can be speeded by addition of certain chemicals, such as soap itself. The physicist says such materials "lower the surface tension" of the washing solution.

After the dirt has been loosened by wetting, the carbon or other solid dirt particles must be deflocculated. Think of how a flock of ducks act when a hunter fires at them. They fly away in all directions; the flock is completely broken up. That is what happens when a lump of dirt is deflocculated. The dirt particles scatter but, unlike the ducks, they cannot easily reassemble into a single group because the scattering is due to electrical charges on the particles which act to repel each other.



HYDRATED POWDERED SILICATE ($Na_2O{\cdot}3.2SiO_2$) MAGNIFIED 150 DIAMETERS

If there is oil or grease in the soil it must be emulsified, that is, broken up into tiny droplets and distributed throughout the solution in such a way that it will not float to the surface to form a greasy layer which would film out on dish or cloth as it was removed from the solution.

All of these things, wetting, deflocculation, and emulsification, are done well by silicate of soda and so the makers of soap put it in their products in order that you

SILICATE GLASS AND POWDERS

may be able to wash dishes more rapidly and get them cleaner than you could if you had only pure soap to help you. For additions to soap the preferred silicate is $Na_2O{\cdot}2SiO_2$.

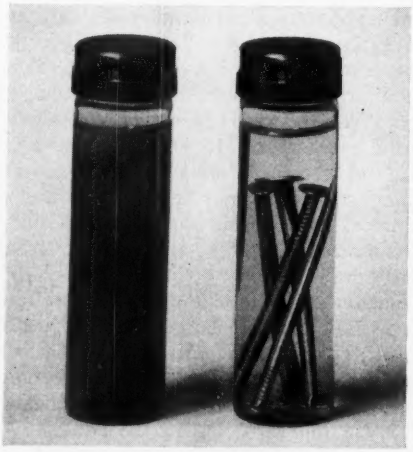
If your clothes are washed at a commercial laundry it is quite probable that another special silicate is used on them. Most laundrymen prefer sodium metasilicate ($Na_2O{\cdot}SiO_2$) for this purpose. It is quite alkaline and must be used cautiously but it has certain advantages. This grade is a true crystalline material and is made by combining caustic soda (NaOH) with a silicious liquid silicate and allowing the metasilicate to crystallize out. It looks like table salt, dissolves about as easily. The laundryman sprinkles it directly into the wash wheel and observes an immediate increase in the volume of suds. He likes the improved whiteness of the clothes which are washed with this material, although he possibly does not realize that one of the reasons for this is that the sodium silicate has the special ability of preventing suspended dirt from redepositing on the clothes. This is an extremely important factor in washing clothes and is one of the reasons why soaps are "built" with silicate of soda.

There is another washing problem of commercial importance though you may be surprised to learn of it. What is the shiny metal on the lamps and bumpers of your family automobile? "Chromium," you say. Yes—chrome plate. And there is probably a great deal of other metal-plated work around you. Perhaps your watch is gold-plated. The knives and forks on your table may be silver-plated. The lamps in your living room may be plated with brass or copper. Certainly you have numerous cans of fruit and vegetables in your kitchen which are tin-plated. "Tin cans," as they are commonly called, are really sheet steel plated with tin.

You know that this plating is done electrically, but did you realize that if the plating is to be at all permanent the base metal must be scrupulously clean; there must be no trace of grease or oil? Even the slight oil film of a thumb print will prevent proper adherence of the plating. To bring metal to this condition it is washed in a highly alkaline silicate. Either the orthosilicate, $2Na_2O{\cdot}SiO_2$, or the sesquisilicate, $1.5Na_2O{\cdot}SiO_2$, are used. Often the cleaning is done electrochemically. A continuous ribbon of steel, for instance, may travel at the rate of two hundred feet per minute through a bath of metasilicate carrying a strong electric current. Cleaners must be very efficient to do good work at that speed.

In industrial work it is often necessary to wash equipment made of aluminum or tin, which normally are attacked by strong alkalies. The presence of silica in the molecule has a protective action on these sensitive metals and therefore the silicates are basic ingredients in most cleaners intended for service in dairies, bakeries, and food packing plants which use large quantities of such metals.

We have mentioned the adhesive and the detergent uses of silicates. Another major use is in cements. When the furnace in your home was installed the fire pot was probably given a lining of a cement made from clay and a silicate of soda ($Na_2O{\cdot}2.4SiO_2$). Under furnace heat this bakes to a hard, stone-like condition which helps metal or firebrick to resist the disintegrating attack of furnace gases. Huge industrial furnaces must often be given similar protection. Other cements are used to give acid resistance. Chimneys for smelters, carrying very corrosive gases, may be lined with a mixture of powdered silica and a very silicious silicate



ANTICORROSION: IRON NAILS IN WATER
Left, no silicate; *Right*, 50 ppm 1:3.2 silicate

($Na_2O{\cdot}3.9SiO_2$). In Mexico there is a chimney 450 feet high which was lined with this mixture. An entire carload of sodium silicate was consumed in that single project.

There are many other uses for silicate of soda. The paper on which this is printed may have been sized by an alum-silicate addition to the beater. The sheets on your bed were probably bleached in a combination of peroxide and silicate. The woolen yarn from which your living room rug was made was possibly scoured in a silicate bath. The pipes delivering water to your home may be protected from corrosion by slight additions of silicate to the water. The gasoline for your car was perhaps "cracked" by a process involving a gel made by combining an acid with a silicate; and the well from whence the crude oil came may have been drilled with a silicate-treated mud. The sink in which you washed the dishes was possibly enameled with a silicate containing frit to give improved acid resistance, and the ceramist who made the dishes very probably employed a silicate to deflocculate the clays he used. If you want to know more about the uses of these curious materials you will find references to them in the library, and the manufacturers have booklets in which they are fully discussed.

Away back in the 1600's, when the old alchemical ideas were being rapidly abandoned and the real science of chemistry was beginning, Johann Joachim Becher, a worker in that field, wrote:

> "The chymists are a strange class of mortals impelled by an almost insane impulse to seek their pleasure among smoke and vapour, soot and flame, poisons and poverty, yet among all these evils I seem to live so sweetly that may I die if I would change places with the Persian King."

The wording is a little archaic but the idea is as modern as when it was written in 1669. Perhaps one day you too will belong to "that strange class of mortals." If you should be so fortunate as to find yourself in a field as little known as the soluble silicates, as diversified, as useful—then you too will surely say "may I die if I would change places with the Persian King."

LETTERS

Molecular Weights—Absolute? Relative?

To the Editor:

I enjoyed reading the letter from Thomas B. Coolidge which appeared in the March issue of the JOURNAL OF CHEMICAL EDUCATION, but feel that additional comment is necessary. I agree with Professor Coolidge that clearly defined terms consisting of properly assigned numerical values and precise dimensions are of great importance in the study of chemistry or of any other science. However, I do not agree that his definition of molecular weight is the only definition or necessarily the best. A good definition should be as fundamental as possible, and should not rely on any particular system of physical dimensions.

To my mind there are two meanings to the term "molecular weight," and we should differentiate them as follows:

1. Absolute molecular weight or the mass of an individual molecule.
2. Relative molecular weight or a relationship between masses of equal numbers of molecules.

I would like to state my concept of relative molecular weight by the following definition:

If nM_A is the mass of n molecules of a substance A, and nM_{O_2} is the mass of n molecules of diatomic oxygen, then the relative molecular weight of A, rM_A, is given by

$$rM_A \equiv 32nM_A/nM_{O_2} \qquad \text{[Dimensionless]}$$

where 32 is an arbitrary but convenient dimensionless unit.

From the above definition, it is apparent that relative molecular weight is neither a mass nor a weight, but is a relative number which furnishes a correspondence between masses of equal numbers of molecules.

A convenient unit of mass used in chemical calculations is the mass mol or, as it is generally called, the weight mol or weight molecular weight. If U_m is the unit of mass employed, the mass mol of a substance A, MM_A, would be defined by

$$MM_A \equiv U_m rM_A \qquad \text{Dimensions [Mass]}$$

It has been concluded from experimental evidence that for any choice of a mass unit, such as gram, pound, ton, etc., the mass mol consists of a definite (not arbitrary) number of molecules. This number, which I shall designate by N_{U_m}, furnishes us with a connecting link between relative molecular weight and absolute molecular weight. If aM_A is the absolute molecular weight, then

$$aM_A = \frac{MM_A}{N_{U_m}} = \frac{U_m rM_A}{N_{U_m}} \qquad \text{Dimensions [Mass]}$$

The definitions given above certainly work, and I feel that they are clear and precise.

WESLEY E. BRITTIN

UNIVERSITY OF COLORADO
BOULDER, COLORADO

Adventures of Kekulé—Brooklyn Style

To the Editor:

In my class in organic chemistry there is a boy with a very fine sense of humor, and he is not going to let the austere subject of organic get him down.

On a term test the other day, the class was asked to discuss "The Benzene Problem." This student's

answer to that is clever enough so that I thought you could use it in the JOURNAL.

"By the benzene problem is usually meant the problem of benzene. Whereas books have been written on this subject (among these the work of Schnoud and the excellent dissertation of Ebbing and Stahfen are recommended to the sincere student) I will confine myself to a few golden words.

"Ya see, de trouble is, wot yuh gonna do wit de unsaturated linkages, huh? If you make her a straight-chain job, den you're nonplussed coz she don't react wit poimanganate, not even coincentrated, see? So dis guy Kekulé he's sleepin' off a bad one, see, and he dreams up dis ring idea, and he pops it down on paper and den goes out like a light. Well, when he wakes up in de morning he swears he'll never touch anudder drop, see, specially after he takes a squint at dat crazy ring he drew de night before.

" 'Why,' says he, 'anybody dat nose anyting nose dat dere ain't no isomers of meta-dichlorobenzene, dere's only one.'

"And so, jest to forget about de whole ting, he kicks de gong aroun' again, and dat's when he dreams up de oscillatin' bonds, see, and when he sees wot he's done de next morning he goes to his liker closet and trows away a whole lot of Scotch, see. Well, you asked for her; dere she is, in a nutshell."

That seems to sum up the benzene problem very adequately.

CROOM BEATTY, III

ROLLINS COLLEGE
WINTER PARK, FLORIDA

Three!

To the Editor:

This is to register my interest in both your "Editor's Outlook" and "Origin and Transformation of Carbohydrates in Plants," as carried in your January issue.

As a member of the American Chemical Society and a teacher of chemistry on both the high-school and junior college level the following comments may be of some interest.

Low membership in the A. C. S. among teachers of high-school chemistry might be partially due to the following:

1. Lack of concern on the part of the A. C. S. for the high-school teacher, his welfare, and his teaching conditions. Chemistry is being taught in too many schools by teachers who are not properly prepared, and in laboratories (or without laboratories) that are not properly equipped. The A. C. S. could bring pressure to raise the professional level and improve the conditions of the high-school teacher of chemistry. This done, memberships will come in.
2. More could be offered for the benefit of high-school teachers in the publications of the A. C. S.
3. The A. C. S. should do more missionary work to make these non-member teachers of chemistry aware of values available in the A. C. S. publications and membership.

As a teacher in a small school where my duties range from high-class janitor work through Civilian Pilot Training to the teaching of chemistry, I can understand the difficulty of digging up the membership dues each year, but I can testify that the publications and the pride of membership do produce ample returns in teaching results.

M. J. MILES

DIXIE JUNIOR COLLEGE
ST. GEORGE, UTAH

Editor's note: There has been no "lack of concern on the part of the A. C. S. for the high-school teacher"; rather has there been a feeling that little or nothing can be done about the present conditions. The result of a careful study of this matter by a committee of the Council of the Society was published in the *News Edition* of *Industrial and Engineering Chemistry*, **14**, 147 (April 20, 1936). Copies of this report can be had from the Secretary of the Society.

FOURTH SUMMER CONFERENCE OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

PRELIMINARY ANNOUNCEMENT

FOLLOWING three successful Summer Conferences, the New England Association of Chemistry Teachers is making plans for the Fourth, to be held this summer on the campus of the University of New Hampshire, Durham, New Hampshire, on August 11 to 14.

The central feature of the program will be a symposium on "Atomic Structure," headed by Dr. J. E. Cavelti of Allegheny College. A number of well-known speakers have been invited to participate in the program. Round table discussions and papers pertaining to the teaching of chemistry in secondary, junior college, and college grades are planned.

There will be a small registration fee; meals and lodgings will be provided at a minimum rate by the University; and accommodations for families will be available. A social program has been planned.

For further information, letters should be sent to the chairman of the committee, Millard W. Bosworth, Vermont Academy, Saxtons River, Vermont.

CORRECTION

A CORRECTION for "The Home Preparation and Preservation of Food," in the March, 1942, issue, page 140: The last three and one-half lines should read "and the production of sauerkraut requires that lactic acid bacteria be present before the sugars present in the cabbage are converted into lactic acid."

Out of the Editor's Basket

SISTER Ann Cecile tells us that in the course in elementary chemistry at Marymount College, Salina, Kansas, they recently wanted to illustrate the Tyndall effect in colloidal solutions. Not having a suitable illuminator for the purpose, they devised one out of a No. 2 Brownie box camera by removing the film support and spools and putting a 75-watt electric light bulb in the box. Using the smallest diaphragm opening and setting the shutter for time exposure gave a very satisfactory light cone in a darkened room.

● The recent catalog of the Coleman Electric Company contains two items which struck us as unusually interesting. The first of these is a line of medical glass electrodes which may be inserted directly into wounds, tissues, nasal passages, etc., to determine pH. One may indeed be swallowed and the pH of stomach or intestines determined *in situ*. A recording instrument may even be used to get continuous measurements all the way down!

The other feature is a photometer which contains its own light source and which may be clamped upon the ear of the subject. An electric recorder shows changes in the color of the blood in one of the ear veins, from which may be calculated the ratio of oxidized to reduced hemoglobin in the blood stream. This instrument is expected to have important applications in aviation, oxygen therapy, and anesthesia, and was invented by Dr. Glenn Millikan, of the Cornell Research Foundation, which holds the patents for it.

● There will be an unusual variety of summer courses offered at the various colleges and universities this year. As a result of their "accelerated programs" many institutions will offer summer work which have never done so before. In addition to the common six-week "summer sessions" there will be two-period sessions of six weeks each, full-length semesters of twelve and fourteen weeks, intermediate, eight-week courses, and various other combinations. Starting times will vary from the first of May to the last of June.

In view of the evident need for haste in our national production no student should interrupt his chemical training, if it can possibly be avoided. Moreover, the incoming classes of freshman chemists should be started immediately and many institutions are making all possible efforts to do so. It can scarcely be overemphasized that this is no time for idle vacations. Furthermore, the future of the Selective Service draft is still uncertain, and young men who want a college education—in any field whatever—before being taken into military service, will do well to get started at it as soon as possible.

● We recently received a very up-to-date little pamphlet in Spanish on the Classification of the Elements (Clasificación de Elementos) by P. E. Chiancone. It consists, principally, of an excellent chart of the Periodic Table and a clear exposition of its significance in terms of atomic structure. We were unable to tell the source of its publication, but its appearance emphasizes again the desirability of closer coöperation with our Spanish-American neighbors.

● Recent figures from the Office of Education show that war in many countries of the world has brought larger numbers of foreign students to the United States during the last year. Colleges and universities have requested the Office to evaluate credentials of 1158 students from 70 different countries.

● We think the following quotations are pertinent, having to do with the interaction of education and the war:

"The navy does not ask you to change your curriculum or revolutionize your schedule to turn out fighting machines. In fact they do not even ask that you give any kind of military training. The kind of instruction that is useful to the armed forces is the very kind of instruction that will be of most use to the citizen in the peacetime world that is to follow. It is striking evidence of the impeccable rightness of our fight that the subjects which help America wage the war are the subjects which will help build the peace after the holocaust is over. How, then, can you help? First, and foremost, you can help the navy immeasurably by the simple expediency of stressing those of your regular subjects in which the navy has found its present recruits most lacking. Mathematics is the most important of these, followed closely by sciences and manual subjects."
—PAUL C. SMITH, Lieutenant Commander, United States Navy

"We educators know that the easiest way to lose a football game is to have a team that breaks training rules and that will only half prepare for a contest. It is often the last minutes of a game that are decisive; the players who can come through then are the winners. Anyone who thinks that a night club is a place to prepare for an all-out war has another think coming, if capable of another think."
—RAY LYMAN WILBUR, President, Stanford University, California

"Vast changes must be introduced into the curriculum to help change attitudes built around an earth-bound civilization into attitudes that also include life in the air. To some extent the step may be taken through separate courses in the schools on various phases of aviation. But also, it probably will be accomplished through infiltration of the various phases of the subject of aviation into practically all the courses of study."
—ALEXANDER J. STODDARD, Superintendent of Schools, Philadelphia, Pennsylvania

"I wonder if we realize fully that all of this business of expansion and acceleration that occupies so much of our time and attention is not going to stop when the war is won; that much of it is not as temporary, for the duration, as it may seem to be."
—JOHN LUND, U. S. Office of Education, Washington, D. C.

● The supplies of both spermoil and coconut oil have been largely cut off, due to war developments. The former of these was principally obtained from the

whaling fleets of Norway and Japan, operating mostly in Antarctic waters. Spermoil is invaluable as a "breaking in" oil for airplane and other high-speed motors and most of the available supply is now going to that use.

Coconut oil has been put on a priority basis because of its especially high glycerin content. Large quantities of it were previously obtained from the Far East.

Both these oils, however, have a large use in the tanning industry and their virtual elimination from the market has resulted in the development of substitutes. One of these is known as Tanoyl, produced by leather chemists at the National Oil Products Company.

● In 1940 the United States turned out 412,560,000 pounds of aluminum. The estimated output in 1941 is in excess of 600,000,000 pounds. The Westinghouse "ignitron" helped make this increase possible because of its ability to change alternating current electricity into direct current, essential to the electrochemical process that produces aluminum from purified mineral bauxite.

Ignitrons also are aiding the recovery of magnesium from ocean water. Magnesium hydrate taken from the ocean is converted into magnesium chloride and reduced to magnesium by an electrolyzing process employing ignitrons. Chemists have estimated that about four and a half million tons of magnesium can be recovered from a cubic mile of sea water.

Suspended in the ignitron's steel tank is a graphite electrode connected to the alternating current supply. In the bottom of the tank is a shallow pool of mercury. Fastened above the pool is a one-inch pointed piece of boron carbide the thickness of a pencil. This dips into

POWER FOR ALUMINUM PRODUCTION IS SUPPLIED BY THIS LINE OF IGNITRONS WHOSE TOTAL RATING IS 60,000 AMPERES AT 645 VOLTS D.C.

the mercury and is the spark plug or igniter that makes the ignitron work.

In operation, positive electricity from the alternating current power line is conducted to the graphite electrode in the top of the ignitron tank and also to the igniter. The instant this positive electricity reaches the igniter it forms a spark or "cathode spot" on the mercury pool and permits the power current to flow. When the current changes to the negative phase, the rectifying property of the mercury vapor prevents any discharge from passing in the reverse direction.

● The manufacture of fibered glass starts with $^3/_4$-inch diameter highly refined glass marbles which are melted and the liquid glass allowed to flow through 204 tiny holes. The resultant filaments are so fine as to be nearly invisible. They are then gathered together to form a continuous filament 97 miles long. Continuous fibers as long as 5000 miles have been made.

● To find out how oxygen combines with metals, and how fast, Dr. Earl A. Gulbransen, of the Westinghouse Research Laboratories, is weighing oxide films, or rust, with a tiny weighing machine so sensitive it measures its loads in weight units of ten billionths (10/1,000,000,000) of an ounce. Each year rust, tarnish, and corrosion cause an estimated 200 million dollars damage to bridges, steel buildings, and machine parts. Through this research, Dr. Gulbransen is seeking new ways to protect steel and other metals against the destructive action of oxygen in the air.

The special weighing machine devised for this study is sealed in a glass tube to take measurements on pieces of metals half the size of a razor blade. Movements of the balance's pointer, so minute they can be observed only through a microscope, reveal the weight added to a tiny sample of steel by a single layer of oxygen atoms.

● The Charles A. Coffin Fellowships are granted annually by a foundation established by the General Electric Company, to enable outstanding graduates to undertake or continue research work in educational institutions in this country or abroad. The awards made this year include one in the field of chemistry, to Hershel Markovitz, of the University of Pittsburgh. The remaining four are in physics: to Boris D. Abramis, University of California; Robert W. Hull, Yale University; Edward R. Kane, Union College; Arthur E. Snowdon, Carnegie Institute of Technology.

● Edmund E. Day, in discussing issues confronting higher and professional education, in the February number of the *Journal of Higher Education*, brings up one point which is especially important right now. He says:

"The Pennsylvania Study of the Carnegie Foundation brought out clearly the fact that, of the better half of high-school graduates, only about one-half go on to college, and, of the students who do go to college, about one-quarter are less qualified for higher education than one-half of the high-school graduates who do not succeed in going on to college. In other words, much of the student material the colleges get is inferior, and much of the student material that is superior the colleges do not get. . . . What we must have is both an improved technical procedure and an improved administrative organization for the selective handling of students at all levels."

● Everything must be done to help people find their proper jobs in this war. In this connection we like especially the remarks made by Watson Davis, Director of Science Service, in a recent address:

"We must begin an intensive search for genius, or at least, superiority in science. Those who have been endowed by nature and their ancestors and by their training and environment with a flair for science and research must be allowed to use that ability to the best interests of our war effort and our civilization. We must see to it that the unusual boy or girl gets an opportunity to go to college or technical school and is channeled into a definite specialized responsibility in our growing national machine for fighting and producing. We must see to it that the exceptional boy or girl is given the basic education that will allow him to become a leader in the important reconstruction after the war.

"This may mean a new viewpoint upon scholarships and fellowships. It may be necessary and advisable to pick the promising individuals while they are still in high school or even earlier and then assure them the training most useful to our national effort, regardless of whether their parents are rich or poor. This may be an activity in which industries should be interested or it may be a matter of governmental concern to the same degree as training airplane pilots or fighting men.

"This search for genius in science is a part of the great task of selective service in which during the coming months and years we shall all have the opportunity and duty to engage."

● The remarks we made in the February number concerning the National Teacher Examinations may have seemed somewhat disparaging. We have since seen a more complete account of the examination and its results, which brought out certain points not before apparent. This examination was taken by 4718 candidates for teaching positions, of whom 100 were secondary-school physical science teachers. One part of the examination was common to all candidates, another consisted of subject matter in the field of specialization. In only two items of the common examination did the physical science group fall before the average for all teachers: literature and English expression. Only the mathematics teachers had a slightly higher total score on the common examination than the physical science group. It was to be expected that the latter group would rate high on the scientific and mathematical sections, but, strange to say, they also did better than average on contemporary affairs, current social problems, and history and social studies.

The results of the section devoted to specialized subject matter showed that when science teachers are called upon to teach a combination of such subjects as physics, chemistry, and general science, there is need of a balanced background of training in several of the physical sciences. In general, the figures indicate that candidates who have been trained in both biological and physical sciences are somewhat better prepared in each of these fields than are those whose major fields are more diverse.

● We were pleased to note recently that our "Editor's Outlook" in the February number, as well as the "Ten Questions" which accompanied it, were read into the *Congressional Record*. Although we have a profound respect for the *C. R.* and appreciate the honor bestowed on the JOURNAL, we doubt if this will bring our remarks to the attention of a large number of people! (Did you ever see a "cover-to-cover" reader of the *C. R.*?)

● About a year ago the Federal Civil Service Commission began a recruiting drive for technologists. The number of persons on the employment lists now established is not sufficient for today's wartime needs. Accordingly, the Commission has recently reissued the announcement of these opportunities for Government employment with slightly modified requirements. Salaries for the positions range from $2000 to $5600 a year. Applications may be filed until further notice with the Commission's Washington office.

By technologist the Commission means a person experienced in "the necessary production, engineering, and scientific research work essential for the successful operation of an industrial plant, where such plant operation is based upon a thorough and expert knowledge of a branch of an applied science," such as explosives, fuels, plastics, rubber, minerals, or textiles.

● We recently had an opportunity to see one of the latest sound productions of Erpi Films, entitled "Chemistry and a Changing World." It struck us as very well suited to its purpose, which is neither to impress one with the "marvels of chemistry," nor to inform one minutely on chemical theory or technology. Its aim is to show the steps that are necessary, by way of research and development, in the complete establishment of an industrial chemical process. The modern method of manufacturing phosphoric acid is the example chosen.

SUMMER COURSES IN MICROCHEMISTRY AT CORNELL UNIVERSITY

DURING the coming Summer Session, June 29 to August 7, the Department of Chemistry at Cornell University, Ithaca, New York, will offer courses that may be taken separately or in combination, as the time and needs of the student justify.

Quantitative Microanalysis will cover inorganic and organic procedures according to the methods of Pregl and others. Enrolment is limited, and inquiries should be addressed to M. L. Nichols.

Introductory Chemical Microscopy will include studies of particle size, optical properties and physical chemistry of crystals, lens systems and photomicrography, and applications to technical materials. Microscopical Qualitative Analysis will cover the common inorganic anions and cations. Inquiries regarding these courses or a shorter term of study should be addressed to C. W. Mason.

RECENT BOOKS

pH AND ELECTRO TITRATIONS. The Colorimetric and Potentiometric Determination of pH. Potentiometry, Conductometry, and Voltammetry (Polarography). Outline of Electrometric Titrations. *I. M. Kolthoff*, Ph.D., Professor and Head of Division of Analytical Chemistry, University of Minnesota, and *H. A. Laitinen*, Ph.D., Instructor, University of Illinois. Second Edition. John Wiley and Sons, Inc., New York City, 1941. ix + 190 pp. 43 figs. 15 × 23 cm. $3.00.

The present edition is such a considerable enlargement and so thorough a revision of its predecessor that it seems like a different book. A completely new section on "Voltammetry (Polarography) and Amperometric Titrations" has been added as Part 4 to the three parts of the earlier edition. These covered: Acid-Base Equilibria and the Colorimetric Determination of pH, The Potentiometric Measurement of pH and Potentiometric Titrations, and Conductometric Titrations.

The book embodies the subject matter of three one-quarter courses offered to seniors and graduate students at the University of Minnesota and is intended to accompany two lectures and four hours of laboratory work a week. Anyone who presents this material will find the book exceedingly valuable both for routine reference and as a students' text.

It is especially as a guide to laboratory work in this field that the book will prove valuable, as most of the other works on these subjects are written for research workers rather than for students. The new fourth part is distinctly a pioneering venture, and is at present the only thoroughly convenient collection of most of the material on the polarograph and amperometric titrations.

The emphasis throughout the book is on the simpler types of apparatus which are likely to be accessible in almost all laboratories, or are easily constructed. The expensive and complicated modern polarographs, spectrophotometers, and conductance bridges are barely mentioned. The treatment of acids and bases in aqueous solution in the first chapter skilfully combines the Brønsted-Lowry definitions with the treatment of hydrolysis along classical lines, and a sufficient use is made of the formulas of the Debye-Hückel theory of interionic attraction to serve the needs of elementary students. A good selection of problems concludes each chapter, and a four-place logarithm table is included. The makeup of the book is excellent and there seem to be comparatively few minor errors.

NORRIS F. HALL

UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

INTRODUCTORY CHEMISTRY WITH HOUSEHOLD APPLICATIONS. *Nellie M. Naylor*, Associate Professor of Chemistry, Iowa State College, and *Amy Le Vesconte*, Professor of Chemistry, Mary Hardin-Baylor College. Revised Edition. D. Appleton-Century Co., Inc., New York City, 1941. xv + 476 pp. 59 figs. 13.5 × 20.3 cm. $3.25.

This is a good, easily readable, and thoroughly modern text published in the James Kendall Century Series of science texts. The authors have done a good job of writing a book for "a middle course between making a subject too practical and making it too theoretical." The book, as stated by the authors, has been written primarily for students of home economics. Therefore many of the illustrations given are drawn from experiences common in the home. Except for these references, however, and a few such chapters as "Chemistry in the Laundry," "Leavening Agents," and parts of such chapters as "Water and Its Uses" and "The Colloidal State," the content of the book is very much that of any modern text in general chemistry. Although there is no such detailed discussion of metals and their compounds, for instance, as is found in most texts in general chemistry, alloys, on the other hand, receive good, and fuller treatment than in many introductory texts. However, many of the laws and theoretical principles of chemistry are not treated in as thorough and detailed fashion as is common in most college texts.

There is nothing strikingly new in the order of presentation of material, but in this connection there may be mentioned a point of interest to teachers who do not wish to follow the order in any available book. The very fact that some of the theories and laws are treated in less detail than is usual will make it easier to use this book than most texts, in a course which does not follow a prescribed sequence of topics. The book outlines a rather descriptive course, but the questions at the ends of the chapters indicate that the authors expect the instructor to carry the discussions much further than the text does and to use the latter as background material.

The many questions at the end of each chapter are among the better features of the text; they are very well chosen and incorporate sound principles of pedagogy. Also, there are 151 supplementary questions at the end of the book, grouped so that each set covers the material of several chapters, which constitute good review questions. There is also a bibliography of journal articles and extracts from books at the end of each chapter. These include ample references to allow considerable choice on the part of the instructor or student.

As indicated, well-organized descriptive material is given somewhat more prominence in the book than are the discussions of the fundamental laws and theoretical principles of the science of chemistry. For instance, the subjects of chemical and physical equilibrium receive abbreviated treatment, but such material as is included is thoroughly up to date. The way in which this material is handled seems, in many instances, to encourage the student to work too much on a memory basis. Too often some of these fundamental laws and principles appear as somewhat isolated material which may not always seem quite essential in the text; or rather, the information does not always seem to be a necessary working tool for the subsequent material of the course. But, according to the authors "fundamental chemistry" does receive more extended treatment in this edition than in the former one. The "middle course" is not an easy one to achieve.

HARRIETT H. FILLINGER

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PHOTOGRAPHIC EMULSION TECHNIQUE. *T. Thorne Baker*, F.R.P.S., A.M.I.E.E., F.Inst.P. American Photographic Publishing Company, Boston, 1941. xii + 263 pp. 78 figs. 14 × 20 cm. $4.00.

This is a book for the advanced, experimental amateur in photography rather than for the casual hobbyist. Research men and photographers interested in the properties of emulsions and their manufacture will find it extremely valuable.

The author's extensive experience has enabled him to include a large amount of plant practice and empirical data not available in assembled texts or in the general literature. Commercial operations are described and scaled-down counterparts of these are given for the use of the laboratory emulsion maker. These are presented in careful detail. The chemist-experimenter will be particularly fortunate in that much of the required apparatus and materials are already available to him.

The topics treated include a brief history of the development of gelatin emulsions, specifications and handling of emulsion materials, preparation of plate, film, paper, and special emulsions, fine grain, slow, rapid, and color emulsions, special development and printing operations, and the testing and control of emulsion quality. Many simple sketches and tables are used to supplement the text.

CHARLES E. RENN

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CAMBRIDGE, MASSACHUSETTS

THE THEORY OF RATE PROCESSES. *Samuel Glasstone, Keith J. Laidler,* and *Henry Eyring,* Princeton University. First Edition. McGraw-Hill Book Co., Inc., New York City, 1941. ix + 611 pp. 137 figs. 15 × 23 cm. $6.00.

The purpose of this book is to describe the development and applications of the theory of absolute reaction rates. To this end considerable space is devoted to the theoretical bases of the subject as well as to a large number of specific cases. Thus there are separate chapters on quantum mechanics, on potential energy surfaces, and on statistical mechanics, including the specialized mathematics required. As might be expected there are extensive discussions of homogeneous and of heterogeneous reactions, of reactions involving excited electronic states, and of reactions in solution. Most commendable is the attempt to show that the theory is really general by applying the same to such phenomena as viscosity, diffusion, and various electrochemical processes.

The authors have performed a noteworthy service not only in this respect, but also because they have coördinated and made available by full discussion so much material that appears only in necessarily condensed journal articles. The literature references are, of course, very numerous. Eighty-seven tables of the most recent data are included by way of illustration.

The book is recommended unreservedly to all who are engaged in rate studies and to those teaching graduate classes in reaction kinetics. The literary style is very good and the format attractive.

MALCOLM M. HARING

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COLLEGE PARK, MARYLAND

PRINCIPLES AND PRACTICE OF CHROMATOGRAPHY. *L. Zechmeister,* California Institute of Technology, Pasadena, late of Chemical Institute, University of Pécs, Hungary, and *L. Cholnoky,* Lecturer at the Chemical Institute, University of Pécs, Hungary. Translated from the second and enlarged German edition by *A. L. Bacharach,* M.A., F.I.C., and *F. A. Robinson,* M.Sc.Tech., F.I.C. First Edition. John Wiley and Sons, Inc., New York City, 1941. xviii + 362 pp. 74 figs. 14 × 21.5 cm. $5.00.

With the translation of this important book into English a gap in our scientific literature has been closed. Although the fundamentals of the chromatographic adsorption technic were developed by Tswett in 1906, it was not until the last ten years that the method became more widely known. Today it has many uses, particularly in the fields of biochemistry and organic chemistry for purposes of purification, identification, separation, and concentration of relatively labile compounds.

The book is divided into a General Section of 88 pages, giving the Principles and Methods, and a Special Section of 228 pages, showing numerous types of applications. These are followed by a bibliography (about 600 references collected to summer, 1938) and author and general indexes. Actually material up to 1938 only is treated in this book, although there are several worthwhile "Notes" added by the translators. Nevertheless some of the outstanding practical applications and theoretical discussions of the past three years are missing. Numerous correlations between adsorbability and structure of certain groups of compounds are given, but the authors point out that "There is, in fact, a lack of theoretical foundations." Since a close relationship undoubtedly exists between chromatography and the more familiar ordinary adsorption studies, it seems strange that no serious attempt was made in this book to correlate these subjects or to incorporate some of the established theories into chromatography.

The student will find in this book adequate discussions of the adsorption media, solvents, eluents, and apparatus, together with a careful description of the experimental procedure, illustrated by numerous photographs, well reproduced. Special technics are further demonstrated by examples in the section on applications. Detailed instructions are given for applications to naturally occurring pigments, synthetic dyestuffs, colorless and faintly colored substances, and to technology. These chapters cover many important compounds such as chlorophylls, porphyrins, carotenoids, vitamins, hormones, sterols, sapogenins, and alkaloids. Finally, examples are also given of inorganic separations by the chromatographic method. Anyone interested or engaged in chromatography will profit by the clear description of the available data and the valuable directions for improvement and extension of the method.

OTTO H. MÜLLER

CORNELL UNIVERSITY MEDICAL COLLEGE
NEW YORK CITY

PHYSICAL CHEMISTRY FOR COLLEGES. *E. B. Millard,* Professor of Physical Chemistry, Massachusetts Institute of Technology. Fifth Edition. McGraw-Hill Book Company, Inc., New York City, 1941. viii + 600 pp. 70 figs. 15 × 23 cm. $3.75.

This excellent text, which first appeared in 1921 and is now in its fifth edition, has been extensively revised and rewritten. The extent of the revision may be judged by the increase in paging from 524 to 600. Within each chapter the subject matter has been rearranged with a more logical sequence and the makeup considerably improved. Perhaps the most obvious mechanical change is the increase in overall dimensions which greatly improves the appearance of the book.

Among the new concepts that have been introduced are those of "ionic strength," "azeotropic" solutions, and "peritectics" as well as the moving boundary method of determining transference numbers. The substitution of the term "standard potentials" for the older "molal electrode potentials" is a welcome change, as is also the use of the encircled negative sign to designate the Faraday equivalent in electrochemical reactions.

The subject of thermodynamics has been considerably expanded and more space devoted to the treatment of the Second Law. The reviewer is impressed by the fact that, notwithstanding the fundamental importance of this subject in physical chemistry, it still is relegated to a minor place in the introductory chapter. Derivations of the van't Hoff isochore and the Gibbs-Helmholtz equation have been included, but the disjointed treatment does not impress the student with the fact that the laws of solutions, of thermochemistry and electromotive force processes are, in fact, outgrowths of the First and Second Laws. It would have enhanced the treatment considerably if a separate chapter had been devoted to thermodynamic principles and their mathematical formulation with emphasis upon the relations that are derivable from them.

The "enthalpy" concept is adopted for general use throughout the book. While the reviewer appreciates the distinction between this quantity and the widely used "heat content," it seems regrettable that the subject must be complicated by such involved phraseology as "molal enthalpy increase of formation." In this day of streamlining, the former "heat of formation," so long as its limitations are recognized or even "molal enthalpy of formation" (which may be either an increase or a decrease) would seem preferable.

The chapters on Solutions (V and VI) and on Equilibrium (VIII and IX) have been greatly improved by appropriate numerical examples illustrating the relationships, to show the student how the principles apply. This is also true of the free energy and electromotive force chapters. A similar treatment of the method of deducing atomic weights from mass spectrographic data and of crystal structure from X-ray data would render those difficult subjects tangible to a student who could scarcely be expected to gain a working knowledge from the brief statement in the text.

The outstanding feature which commends this book is the great variety and excellence of its problems—timely in their significance, well adapted to the needs and ability of the student, and fully half of them new. This splendid book in its present revision should be welcomed by all teachers of the subject.

T. F. BUEHRER

THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

HIGH POLYMERIC REACTIONS. (Volume III of the Monograph Series on High Polymers.) *H. Mark*, Professor of Organic Chemistry, Polytechnic Institute of Brooklyn, and *R. Raff*, Industrial Research Chemist, Howard Smith Paper Mills, Ltd., Cornwall, Ontario. Translated from the manuscript by *L. H. Weissberger* and *I. P. Irany*. Interscience Publishers, Inc., New York City, 1941. xiii + 476 pp. 49 figs. 15 × 23 cm. $6.50.

As the authors' division of this monograph into a general section and a special section indicates, its purpose is twofold; first, to present the field of synthetic high polymers from the general point of view of reaction kinetics and second, to summarize the detailed information now available on over a hundred systems in which polymerization takes place. Historically, the subject is about a century old, as far as isolated observations go; but practically speaking, the chemistry of high polymers is a new subject whose growth is almost entirely due to progress of the last decade, accelerated by the tremendous technical importance of synthetic polymers. As the authors state in their preface, it is still too early to give a final, definitive treatment of the subject; on the other hand, a competent summary of the information now available represents a most valuable contribution to the literature, and will be of very great assistance both to present workers in the field of polymers, and to those who are approaching the subject for the first time. Some idea of the scope of the book will be apparent from the fact that the bibliography includes over nine hundred references to the literature.

The general section begins logically with a treatment of bond energies, and the fact that macromolecules are assemblies of atoms held together by primary valence bonds forms the starting point for the development of the general theory. The fundamental difference between ordinary organic reactions and polyreactions, both of which involve small molecules as reagents, is that the latter give as products compounds of identical elementary composition but of different molecular weights, ranging in order from hundreds to thousands of times the molecular weight of the reagent. The molecular weights of the products are distributed about a most probable value according to a law which is determined by the conditions of reaction. A discussion of distribution of molecular weights thus leads the authors to a discussion of kinetics of reactions, in which chain initiation, chain growth, and chain termination are considered. The difficult task of coördinating familiar concepts in several fields of organic and physical chemistry, and then incorporating into them the recent advances on high polymers is admirably handled. For this reason, the book should be especially useful in the academic field, where insufficient attention has been given to high polymers: industry today needs more graduates who have some familiarity with polymer chemistry. The monograph contains a preliminary scheme for the qualitative identification of an unknown polymer, analogous to Treadwell's analytical tables. In discussing polymerization in gases, liquids, and emulsions, and in describing the progress of polyreactions, many details of experimental methods are given. These are adequately supplemented by references to the literature, so that it would be easy to base a laboratory course on the monograph, to accompany a lecture course.

The special section on individual polyreactions covers about five hundred papers, most of which have appeared since 1930. These are discussed from the point of view of general kinetics which was developed in the first half of the book. Hydrocarbons account for well over half of the material in this section; this is, in part at least, due to the fact that the search for synthetic rubber or for rubber substitutes concentrated attention on these compounds. The other polymerizable compounds treated include esters, aldehydes, ketones, halides; the research chemist will find many interesting problems for further work suggested in these pages. A short section on inorganic polymers is also included. Finally, there is an introductory treatment of polycondensations; a detailed account in a subsequent monograph of this series is promised.

RAYMOND M. FUOSS

GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

THIS PHYSICAL WORLD. *C. C. Clark*, Associate Professor of General Science, New York University; *C. A. Johnson*, Instructor in General Science, New York University; and *L. M. Cockaday*, Lieutenant Commander, U. S. N., Military Instructor in Physics, United States Naval Academy. First Edition. McGraw-Hill Book Co., Inc., New York City, 1941. x + 528 pp. 279 figs. 15 × 23 cm. $3.25.

Two types of survey courses in sciences have been in the process of development in recent years. The one is characterized as a critical appraisal of scientific knowledge and the methods by which it has been developed, with the attempt to train the students in the intellectual skills commonly understood as the scientific method. The other is essentially informative, describing the achievements of science and the significance of its application to modern society.

The text reviewed here belongs definitely in the second category. There is a genuine attempt—not always successful—to make the material interesting and inspiring. The brief accounts of economic, historical, cultural, or philosophic significance with which the chapters begin, as well as the excellent photographs, contribute in this direction. The style is simple and "popular."

No serious pretense is made to teach the methods of science, despite the fact that in the introductory chapter the usefulness of the scientific method is indicated. The subject matter is treated with the lack of critical discrimination which is characteristic of popular accounts. Thus, the mechanical operation of the steam engine, the atomic theory, and a version of the planetesimal hypothesis are described as though all three were known (or could be known, for that matter) with the same degree of certainty. Throughout the book one finds categorical statements without an indication of the basis for these statements or an appraisal of their probable validity.

THEODORE A. ASHFORD

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QUÍMICA GENERAL (General Chemistry). *Emilio Jimeno*, Professor of Inorganic Chemistry, University of Madrid. First Edition. Editorial Saeta, Madrid, Spain, 1941. xii + 600 pp. 47 figs. 24.5 × 19 cm. 60 pesetas.

This book is addressed to the Spanish-speaking student of today, who as the chemist of tomorrow will have a share in improving the standard of living of his country. That is why the author dedicates the book to the Spanish and Spanish-American chemist and chemicals manufacturer.

Concepts usually left for more advanced studies have been included in this text because the author felt that, although they require a great initial effort to learn, the wrong ideas require a greater effort to unlearn afterward. The plan of the book is to present fundamental principles, because without them it is impossible to do any serious work in science or in modern applied chemistry. The student is led by the scientific method. The fundamental principles are expressed in a clear, concise, and concrete manner to make their interpretation certain and easy.

The chapters cover the conventional topics in general chemistry and at the end of each is a series of exercises and problems to give the student the opportunity to test his comprehension of the subject matter.

This book should prove useful to:

(1) Spanish-speaking universities, technical and engineering schools, because it is a modern, well and clearly written text, an outline in chemistry.

(2) Industrialists in Spanish-speaking countries, to whom the book may serve as reference and for review, since it contains the modern concepts in chemistry. These usually take many years before finding their way into a general chemistry.

(3) The students of U. S. universities who desire to become acquainted with the Spanish technical terminology, for whom this is a first-class book.

F. R. MORRAL

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STATE COLLEGE, PENNSYLVANIA